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SYNTHESIS OF 1-HYDROXYETHYL-2-DIMETHYL ALKYLAMMONIUM SURFACTANTS AND THEIR PROPERTIES IN AQUEOUS SOLUTION

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SYNTHESIS OF 1-HYDROXYETHYL-2-DIMETHYL ALKYLAMMONIUM SURFACTANTS AND THEIR PROPERTIES IN AQUEOUS SOLUTION

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To my mother Ying-Sheng Liu Chen who encouraged me with her love; to my father late Dze-Bin Chen who taught me to seek and learn; and made my chemical education possible.

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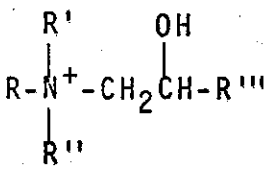
Abstract

A general synthetic method for the synthesis of a new class of chiral surfactants with reactive OH groups was investigated. The surfactants were made by quaternizing the corresponding tertiary amine, in isopropyl alcohol. These surfactants with -OH groups may form tightly-packed non-spherical micelles in the presence of NaOH or alkylamine and these micelles, just like enzyme catalysts, may serve as stereoselective templates. In order to evaluate this stereospecificity, a kinetic study of the reactivity of several chiral reactants in the presence of these micelles, was initiated. The first-order rate constant K for 4-nitrostyrene formation from p-nitrophenethyl trimethyl-ammonium iodide in 0.1 M NaOH at 39°C, increased as a function of surfactant concentration C_s in a manner suggesting micellar catalysis. The data show that N-methyl N-dodecyl 3-hydroxy-piperidinium bromide (DPBr) is a better catalyst than N,N-dimethyl-N-[2-hydroxyethyl] N-hexadecyl-ammonium bromide (CTOH) in the E_2 elimination, probably because it is more hydrophobic. This high activity suggests that chiral surfactants may induce chirality.

PART I

INTRODUCTION

We wish to describe the synthesis of several potentially chiral surface active agents with the following general formula. A polymer containing a similar functional group arrangement is also reported.

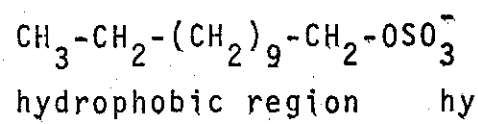


R = alkyl group

In addition we wish to detail the results of our study of the spectral and rheological properties of aqueous solutions of these compounds and since this description requires the use of several terms from surfactant chemistry we will begin our discussion by introducing these terms.[1,2,3]

Fundamental Definitions

Micelle forming surfactants have structures characterized by a hydrophobic region, usually a long hydrocarbon chain, and a hydrophilic region containing a polar or ionized group, e.g. the structure of sodium dodecyl sulfate.



hydrophobic region hydrophilic region

Four principal types of surfactants are commonly distinguished.

(1) Anionic Surfactants:

The anionic part of the molecule is the micelle-forming species, e.g.

sodium dodecyl sulphate (lauryl sulphate)

$CH_3(CH_2)_{11}SO_4^-\ Na^+$

(2) Cationic Surfactants:

The cationic part of the molecule is the surface-active species, e.g.

hexadecyl trimethylammonium bromide

(cetyltrimethylammonium bromide = CTABr)

$CH_3(CH_2)_{15}\overset{+}{N}Me_3\ Br^-$

(3) Ampholytic Surfactants:

This type of surface-active agents can form zwitter ion, and will be considered as either an anionic, cationic or nonionic species by varying the pH of the solution, e.g.

N-dodecyl-N,N-dimethyl betaine (the zwitterionic form)

$C_{12}H_{25}\overset{+}{N}Me_2CH_2COO^-$

(4) Nonionic Surfactants:

This type usually contains hydroxy groups or a poly-oxyethylene chain, e.g.

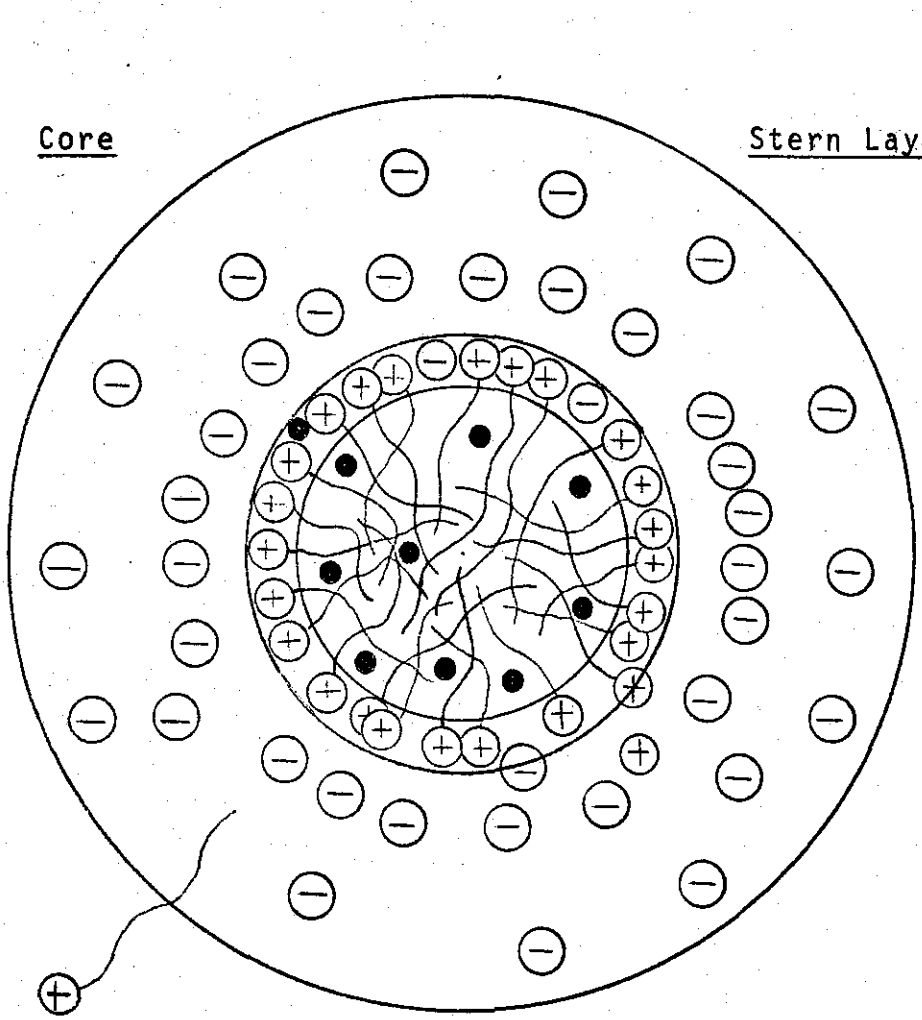
polyoxyethylene-tert octyl phenyl ether

$C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$

When the concentration of a surfactant in aqueous solution exceeds a certain level, surfactant molecules associate to form colloidal aggregates called micelles. The concentration above which these multi-molecular aggregates become detectable is known as the critical micelle concentration or cmc. A schematic representation of an ionic spherical micelle is shown in Figure I. In the center of the micelle are the long paraffin chains so that the center is a non-polar region remote from the solvent, usually water. The polar head-groups are located at the surface of the micelle because they have an affinity for water and will be hydrated by a number of water molecules.

Micelles are not static species but are in dynamic equilibrium with the monomers. It has been shown that micellar break down and build up is very rapid with a half-life in the order of 10 milliseconds. Ionic spherical micelles have average radii of 12-30 Å and contain 20-100 monomers.

Several studies have been made of the shape of micelles. Hartley[1] discussed the possible shape of the micelles in 1939. He suggested spherical micelles with a liquid state interior and a random distribution of counter ions outside. In 1950 McBain[1] proposed two different kinds of micelles: ionic spherical aggregates of less than 10 molecules and nonionic micelles with a lamellar shape. In 1951 Debye and Anacker[1] suggested that micelles could be rod-like. Perhaps



● H_2O Trapped in the Micelle

⊖ Br^- Counterions

⊕ $-\overset{+}{N}(CH_3)_3$ Hydrophilic Groups

⊕~~~ $(CH_3)_3\overset{+}{N}-(CH_2)_{15}-CH_3$

Figure I Structure of a Micelle

the most important and reasonable shape of micelles was proposed by Harkins,[1] who proposed that the shape of micelles can continuously change from spherical micelles (Figure IIa) to lamellar micelles (Figure IIb) and, ultimately, infinitely large "crystals", depending on the pH of the solution, the temperature, surfactant concentration, the presence of additives, and the molecular structure of the surface active agent under consideration.

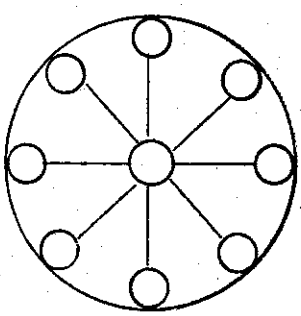


Figure IIa

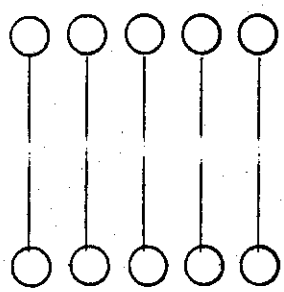


Figure IIb

For detergents containing long chain hydrocarbon groups the cmc value is generally between 10^{-4} and 10^{-2} m/l.[4] A number of methods for determining the critical micelle concentration have been listed by Shinoda.[1] Many physicochemical property changes can be used for the determination of the cmc, but the most reliable common experimental method involves determining the surface tension as a function of surfactant concentration. Below the cmc the surface tension drops with increasing surfactant concentration but remains constant at concentrations above this value. This method was used in this work.

Micellar Catalysis

Micelle-forming surfactants can catalyze or slow down organic reactions. This study furthers the understanding of the factors governing this effect and, by analogy, provides insight into the exceptional catalysis characteristic of enzymatic reactions.

(A) Micellar Catalysis in General

Micellar catalysis is found when reactive molecules, incorporated into the micellar pseudophase, have a greater reactivity than in the bulk solution. In 1959 Duynstee and Grunwald[5] first reported kinetic and equilibrium studies of organic reactions in micellar systems. They studied the effect of cationic and anionic surfactants on the reaction rates of alkaline fading of cationic triarylmethane dyes. The rates of fading of several triarylmethane dyes were accelerated by factors ranging from 1.2 to 18 by the addition of 0.01 M cetyltrimethylammonium bromide (CTABr) and were retarded by factors ranging from 1/4 to 1/75 by 0.01 M sodium lauryl sulfate (NaLS).

The absorption spectra of the dye ions, as shown in Table I, show a significant red shift of the maximum of the visible absorption band whenever the charge of the micelles is opposite to that of the dye ions; but there is no significant shift when the two charge types are the same. These data indicate that there is some interaction when the micelles and dye ions are of opposite charge. The dye ions are incorporated into the oppositely charged micelles.

Table I

Effects of Detergents on the Position of the Maximum of the Visible Absorption Bands in Aqueous Solution[a]

λ max (mμ) of 10^{-5} M Dye

Dye	No detergent	0.01 M NaLS	0.01 M CTABr
crystal violet	592	595	592
brilliant green	630	633	630
malachite green	620	625	620
rosaniline	543	548	543

[a]Data taken from reference 5.

Subseqently,[6] Duynstee and Grunwald employed an organic substrate (triphenylmethane dye, R^+) which exists partly or largely in the micelle phase, and which is capable of reacting either with an anion (OH^-) or with a neutral molecule (HOH). From the kinetic and thermodynamic data, they conclude that an anionic detergent (where the micelles repel the approach of an anion from the bulk phase) suppresses the reaction with hydroxide ion, whereas a cationic detergent (where the micelles attract the attacking hydroxide ion) accelerate this reaction.

Duynstee and Grunwald's study of reaction kinetics in aqueous media containing micelle-forming surfactants stimulated considerable interest. Since that time related studies of micellar catalysis have been frequently published.

In 1967, Menger and Portnoy[7] studied the effect of substrate and surfactant structure on the kinetics of ester

hydrolysis. This study led to a better understanding of the nature of substrate-surfactant interactions in micellar catalyzed reactions. They reported the rate constants for basic hydrolysis of four substrates: p-nitrophenyl acetate (1), mono-p-nitrophenyl dodecandioate (2), p-nitrophenyl octanoate (3), and benzoylcholine chloride (4), in the presence of various concentrations of each of the three surfactants: laurate anion (5), n-dodecyltrimethylammonium cation (6), and n-dodecylpyridinium cation (7).

substrates

$CH_3COOC_6H_4NO_2$ 1

$^-OOC(CH_2)_{10}COOC_6H_4NO_2$ 2

$CH_3(CH_2)_6COOC_6H_4NO_2$ 3

$(CH_3)_3N^+CH_2CH_2OOCC_6H_5$ 4

surfactants

$^-OOC(CH_2)_{10}CH_3$ 5

$(CH_3)_3N^+(CH_2)_{11}CH_3$ 6

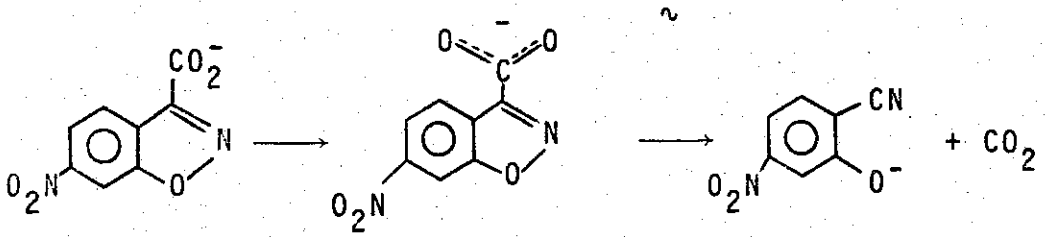
$C_5H_5N^+(CH_2)_{11}CH_3$ 7

Laurate anion (5) forms micelles with highly charged negative surfaces and inhibits hydrolysis of all four esters (1-4); n-dodecyltrimethylammonium cation (6) enhances the rates, and n-dodecylpyridinium cation (7) has very little effect.

The saponification rates of the long-chain esters (2 or 3) are enhanced by the presence of concentrations of n-dode-

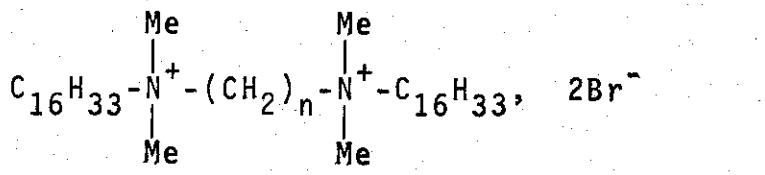
cyltrimethylammonium ion (6) lower than its cmc, but suppressed at higher concentrations of 6. Menger and Portnoy suggested that an ester molecule hydrophobically binds one or more surfactant molecules to form a positively charged complex which reacts readily with hydroxide ion. At concentrations of 6 above the cmc, the ester (2 or 3) is partitioned into the hydrocarbon interior of the micelle where it is inaccessible to hydroxide ion.

Bunton and coworkers[8] examined some electrolyte effects on the cationic micelle catalyzed decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (8).



8

They found that the unimolecular decarboxylation of "8" is strongly catalyzed by micelles of cationic and nonionic surfactants (CTABr, N-cetylpyridinium bromide and Igepal), and unexpectedly, the catalysis by cationic micelles can be enhanced by adding some electrolytes or nonionic surfactants or by using dicationic surfactants, indicating that changes in micellar structure and charge density are responsible for the catalysis. The maximum catalysis by CTABr is 95-fold, by N-cetylpyridinium bromide 100-fold, by Igepal 65-fold; and the dicationic detergent (9a) gives 330-fold catalysis.



9a, n = 4
9b, n = 6

9

Small hydrophilic electrolytes increase the catalysis because they increase micellar size, allowing a closer packing of the cationic head groups and increasing the incorporation of substrate molecules into micelles.

Cordes and Dunlap[9] summarized early work concerning kinetics of organic reactions in micellar systems. They pointed out that the proper choice of surfactant can lead to rate increases of 5- to 100- fold compared to the same reaction in the absence of surfactant.

Morawetz[10] classified all micelle catalyzed reactions into three categories:

(1) Reactions where the surfactant is the only organic reactant.

A typical example is the acid-catalyzed hydrolysis of a homologous series of sodium alkyl sulfates which can form micelles. The reaction rate is independent of the chain length of the alkyl group up to the point at which the reagent forms micelles; beyond this point the reaction rate increases with increasing length of the alkyl chain. This rate-enhancement results from the accumulation of the hydrogen ions at the micelle surface because of the electrostatic potential of the

negatively charged micelle. Correspondingly, the formation of anion micelles results in an inhibition of the hydroxide ion-catalyzed hydrolysis. The uncatalyzed water attack is unaffected by micelle formation.

(2) Reaction between two compounds which are promoted by the electrostatic and solvent effects of the micelle.

Ester hydrolysis falls into this category as do all reactions involving attack of hydroxide or hydronium ion on a solubilized reactant.

Usually those changes in reactivity observed when micelle forming surfactants are added to aqueous solutions of organic reactants are explained in terms of the extent to which both reactants are in the same micelle. When a reaction involves the attack of an ion on an uncharged organic molecule, incorporation of the uncharged species into an ionic micelle will accelerate the process only if the substrate is bound at the micellar surface and the ionic reagent is attracted to the surface because its charge is opposite to that of the micelle. Reactions with ionic species of the same sign as that carried by the micelle are inhibited.

(3) Reactions which are promoted by micelles carrying catalytically active substituents.

We will discuss this in the following sections.

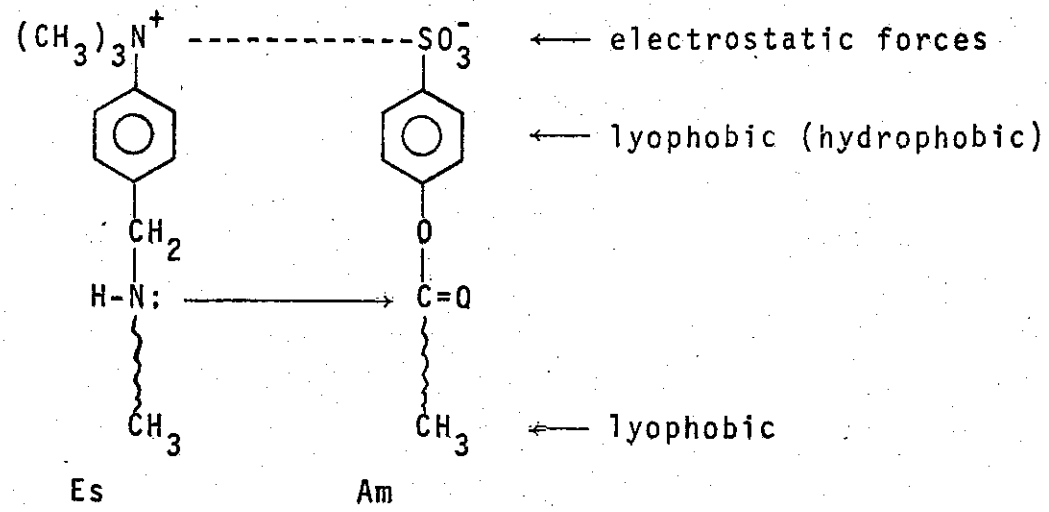
(B) Nucleophilic Surfactants

An especially interesting approach in this area was in-

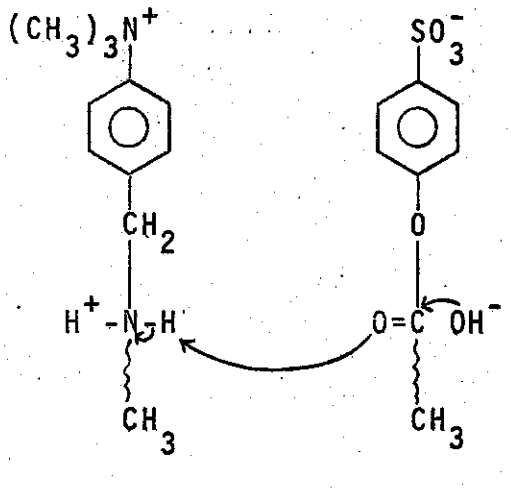
troduced by Bruice,[11] who used detergents containing a nucleophilic group, so that they participated directly in the reaction. Bruice and coworkers examined the rate constants for the alkaline hydrolysis of neutral, positively, and negatively charged esters of varied chain length in the absence and presence of non-nucleophilic and nucleophilic micelles of neutral, positive, and negative charge.

In all cases, increase in concentration of the micelle-forming non-nucleophilic agents resulted in a decrease of the reaction rates for alkaline hydrolysis of the esters. This is due to formation of salts, pre-micelles, and micelles of esters and detergents which either decreases the availability of the ester to nucleophilic attack by OH^- or provides a less favorable media for the hydrolytic reaction. The results are too complicated to be explained here however they do show that nucleophilic surfactants are involved directly in the reaction.

Bruice proposed two mechanisms (I & II) for the reactions of esters (Es) with amines (Am). This study demonstrated the feasibility of designing surfactants with catalytic sites that form micelles exhibiting relative substrate specificity.

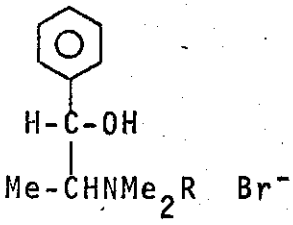


Mechanism I Interaction of esters with amines



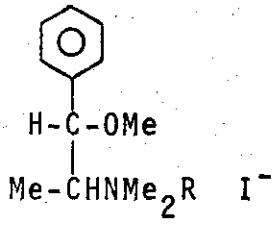
Mechanism II Interaction of esters with the amine conjugate acids and OH^-

Bunton and coworkers[12] have examined micellar effects upon the reaction of p-nitrophenyl diphenyl phosphate(10) with hydroxide or fluoride ions by using the cationic detergents 11 and 12.



11a, $R=C_{10}H_{21}$

11b, $R=C_{12}H_{25}$

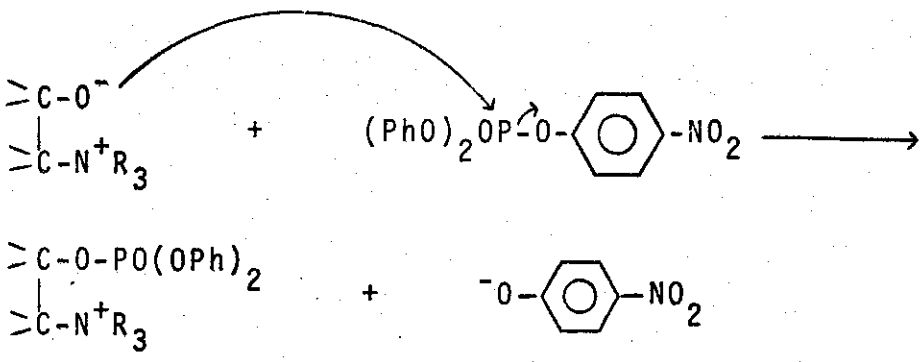


12

They compared the catalytic efficiencies of 11a, 11b, CTABr, and 12 on the reactions of 10 with hydroxide and fluoride ions. Only the hydroxyl group in 11 may act as a nucleophilic reagent, particularly at high pH, where it should be ionized; the methoxy group of 12 would not be especially nucleophilic.

They found that 11b is twice as good a catalyst as CTABr, and nearly four times as good a catalyst as 12. There is no special catalytic activity of micelles of 11 for reactions of fluoride ion. These results show that micelles of 11a and 11b are better catalysts than micelles of CTABr because of the nucleophilic participation by an ionized hydroxyl group in the detergent.

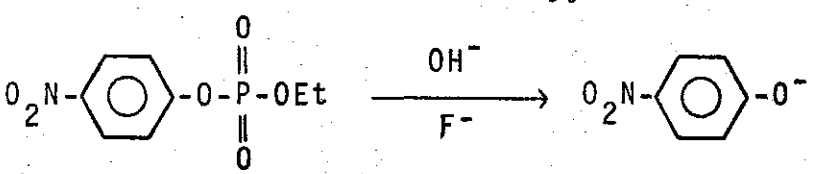
The scheme of this special catalytic effectiveness of nucleophilic detergent 11 in the micellar phase involves the hydroxyl group acting as a nucleophile (especially at high pH, pH $\geq$ pKa = 12.7) attacking phosphoryl phosphorus.



Mechanism III

(C) Hydroxyethyl Surfactants

Later, Bunton and Ionescu[13] described an extension of earlier work[14] with micelles of 1-hydroxyethyl-2-dimethyl-alkylammonium bromides (13 & 14).* The substrates examined were p-nitrophenyl diphenyl phosphate (10), and ethyl p-nitrophenyl phosphate monoanion (15).



15

They reported that micelles of the surfactants 13 & 14 are good catalysts for the hydrolysis of 10 & 15 in the presence of hydroxide ion, causing over a 300-fold rate enhancement of hydrolysis of the triarylphosphate in the presence of 14. This catalysis, and the variation of the reaction rate with hydroxide ion concentration are due to nucleophilic participation by the alkoxide ions of 13 or 14. The pKa values for the hydroxyl groups of 13 and 14 were

---

* Structure for 13 and 14 are given in Figure III.

found to be 12.4 and 12.9 respectively.

The catalytic effectiveness of nucleophilic and non-nucleophilic surfactants for reactions of hydroxide and fluoride ions is illustrated by the maximum rate enhancements relative to reactions in the absence of surfactant at 25°C. The maximum enhancements of the second-order rate constants for the reaction of phosphate esters with 0.01 M NaOH or NaF are given in Table II.[13] (The surfactant concentrations required for maximum catalysis are given in parentheses).[13]

Table II

Rate Enhancements for Reactions with Hydroxide & Fluoride Ions[a]

	Surfactant			
Reaction	$C_{12}H_{25}NMe_2Br$	CTABr	13	14
$ArOPO(OPh)_2$[b] + OH^-	4.8(0.015)	12(0.003)	8.3(0.012)	310(0.002)
$ArOPO_3Et$ + OH^-		6.3(0.01)	29(0.025)	86(0.015)
$ArOPO(OPh)_2$ + F^-	10.5(0.015)	35(0.002)	13(0.015)	52(0.003)
$ArOPO_3Et$ + F^-		4.6(0.015)	4.2(0.02)	

[a] Data taken from reference 13; see text for details.

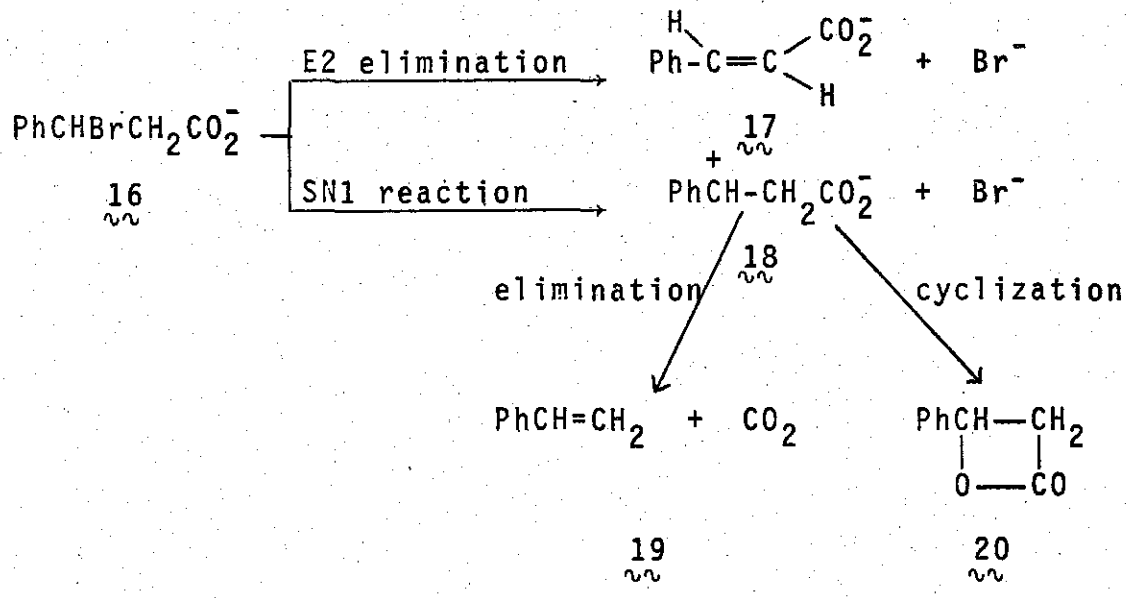
[b] Ar = O_2N- C_6H_4-

CTABr & 14 catalyze the reactions of esters with fluoride ion to similar extents but 13 is always a much better catalyst than CTABr for reactions with OH^-. The reactions of di- and trisubstituted phosphate esters with hydroxide

ion in the presence of the nucleophilic surfactants (13 & 14) also follow mechanism III.

Bunton also showed that the micellized alkoxide ions derived from 11b are less nucleophilic than those from 13. The observed rate constants in 0.01 M NaOH were 0.6 and 3.0 sec^{-1} for 11 and 13 respectively. This difference in nucleophilicity is due to the steric and electronic effects of the phenyl group.[14] The choline anion is approximately 35 times as reactive as hydroxide ion toward 10, and this high reactivity is also shown by its micellized derivatives 13 and 14.

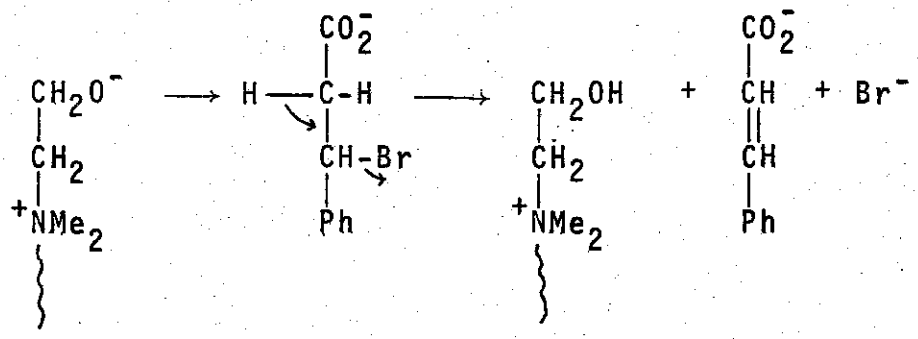
Bunton, Kamego and Ng[15] have examined micellar effects on the decomposition of 3-bromo-3-phenylpropionate ion (16) in the presence of the hydroxyethyl surfactants 13 and 14.



In dilute aqueous alkali styrene (19) is formed by an SN_1 reaction, proceeding via zwitterion (18); the β-lactone (20) is a minor product. While in the presence of the

hydroxyethyl surfactants 13 and 14, even in dilute sodium hydroxide (0.1 M), E2 elimination gives trans-cinnamate ion (17) as the major product, which otherwise appears only in concentrated alkali. A micellized alkoxide ion acting as a good nucleophile was postulated to explain this result.

$$RNMe_2CH_2CH_2OH \rightleftharpoons RNMe_2CH_2CH_2O^- + H^+$$



Since the hydroxyethyl surfactants strongly inhibit the normal bromodecarboxylation via the SN1 mechanism, they inhibit the overall reaction under all the conditions used. Recently, Buton, Minch, Kamego and Wright[16] reported the effect of changes in surfactant structure on the micelle catalyzed spontaneous decarboxylations of 6-nitrobenzisoxazole-3-carboxylate ion (8) and 2-phenylcyanoacetate ion (21).

$$PhCH(CN)CO_2^- \longrightarrow CO_2 + PhCHCN^- \xrightarrow{\text{fast}} PhCH_2CN$$

21

They compared the catalytic effectiveness of cationic (DDTBr and CTABr), hydroxyethyl-surfactant 14, and zwitterionic (22 & 23) surfactants toward the decarboxyla-

tions of 8 and 21. The micellar rate enhancements are summarized in Table III.

$$n\text{-}C_{12}H_{25}N^{+}Me_2CH_2CO_2^{-}$$

22 (glycine derivative)

Table III

Micellar Catalysis of Decarboxylation[a,b]

surfactant	substrate: $PhCH(CN)CO_2^-$ (21)	substrate: CO_2^-, O_2N, N, O (8)
$n\text{-}C_{12}H_{25}N^{+}Me_3Br^{-}$ (DDTBr)	280(0.018)	70(0.012)
$n\text{-}C_{16}H_{33}N^{+}Me_3Br^{-}$ (CTABr)	660(<0.005)	95(0.0016)
$n\text{-}C_{12}H_{25}N^{+}Me_2CH_2CO_2^{-}$ (22)	690(0.013)	170(0.01)
DL-$n\text{-}C_{12}H_{25}N^{+}Me_2CHMeCO_2^{-}$ (DL-23)		210(0.006)
L-$n\text{-}C_{12}H_{25}N^{+}Me_2CHMeCO_2^{-}$ (L-23)		185(0.008)
$n\text{-}C_{16}H_{33}N^{+}Me_2CH_2CH_2OH$ (14)		~ 90
$n\text{-}C_{16}H_{33}N^{+}Me_2CH_2CH_2O^{-}$		~ 200

[a] Values of rate constants relative to those in pure water at 25.0. In the absence of detergent, $K = 9 \times 10^{-7}$ sec^{-1} for the reaction of 21. The values in parentheses are the molarities of surfactant required for 50% catalysis.

[b] Data taken from reference 16.

As shown in Table III, micelles of the zwitterionic surfactant 22 are better catalysts for decarboxylation of 21 than the cationic micelles, DDTBr (dodecyltrimethylammonium bromide), and are slightly more effective than micelles of CTABr despite the shorter chain length. Micelles of the zwitterionic surfactants 22, L-23, and DL-23 cause greater rate enhancements of the reaction of 8 than the cationic micelles, DDTBr and CTABr, despite their shorter hydrocarbon chains.

Micelles of the hydroxyethyl surfactant 14 are effective catalysts for the reaction of 8. At pH 12 the rate enhancement is 90-fold, but at higher hydroxide ion concentrations, 14 is ionized to the zwitterion and the catalysis increases to 185-fold.

$$n\text{-}C_{16}H_{33}N^{+}Me_2CH_2CH_2OH + OH^- \rightleftarrows n\text{-}C_{16}H_{33}N^{+}Me_2CH_2CH_2O^- + H_2O$$

14

The differences in the reaction rates of 8 in micelles of the zwitterionic L- and DL-23 suggest differences in the surface structures of the micelles of the optically active and racemic surfactants. This will be discussed in the next section.

Stereospecific Micellar Catalysis

Moss and Reger[17] explored related phenomena in their study of 1-amino alkane diazotization. They found (Table IV) that the stereochemistry of the deamination of optically

active 2-aminooctane deviates from the "normal" value; ca. 23% net inversion, and moves toward retention when the initial amine concentration exceeds the cmc of the related ammonium ion.

This implies that alkylammonium ion micelles act as agents of stereochemical control. The cmc of racemic 2-aminooctane [$n\text{-}C_6H_{13}CH(NH_3^+)CH_3$] is 0.041 M at pH 4 ($HClO_4$). The stereochemistry of deamination of 2-aminooctane is concentration dependent (Table IV) and alkylammonium ion micelles are responsible for this effect.

Table IV

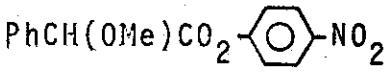
Concentration Dependence of 2-Aminooctane Deamination[a,b]

[2-Aminooctane], M	Stereochemistry
0.76	6% (net) retn
0.39	complete racemization
0.15	7% invn
0.076	18% invn
0.029	27% invn
0.015	23% invn

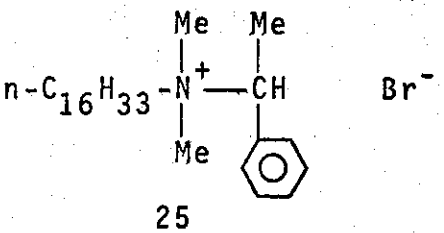
[a] invn = inversion, retn = retention

[b] Data taken from reference 17.

Moss and Sunshine[18] later reported a study of the hydrolyses of optically active and racemic p-nitrophenyl α-methyoxyphenylacetates (24) in the presence of the chiral surfactant (25).



24



25

The rate constants show a significant micellar catalysis, but no substantial stereoselectivity. Surfactant 25 is a poorer catalyst than CTABr for hydrolysis of 24 whereas Bunton had shown that the stereoselective 1-ephedrinium surfactant (11) was about twice as effective as CTABr.[19] Moss and Sunshine concluded that the stereoselectivity caused by chiral surfactant micelle catalysts will increase with their catalytic activity.

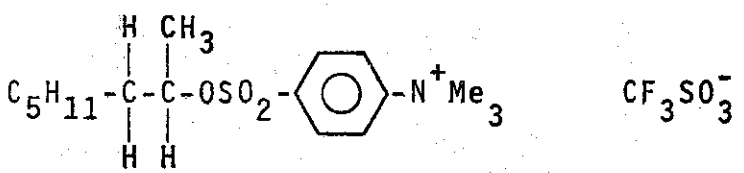
Bunton and coworkers[19] found that the hydrolysis of chiral esters of o-methylmandelic acid (24) is catalyzed stereospecifically by chiral surfactants derived from ephedrine (11). The results show that the D(-) ester is more reactive than the L(+) in the presence of D(-) 11b. The steepness of the plots of $k\psi$ (the first-order rate constant) against detergent concentration suggests that the strongest bonding occurs when the ester and detergent have the same configuration.

Bunton also reported that the DL-ester is less reactive than its enantiomers with D(-) 11b but more reactive than the optically active esters (D(-)24 and L(+)24) in the presence of the non-chiral surfactant CTABr. This suggests that the incorporation of a racemic mixture affects micellar structure

differently than the incorporation of pure enantiomer.

Recently Hindman and Jacobus[20] reinvestigated Bunton's work and suggested that the data are open to a different interpretation. They gave a possible explanation for the previously reported stereochemical differentiation; The individual values of $k\psi$ at fixed micelle concentrations are dependent on the age of the buffer solution. The difference in rate constants may then be caused by the time-dependent pH of the borate buffer solutions.

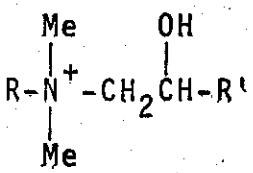
In 1975, Bergman[21] reported a study of the effect of micelle formation on the rate and stereochemistry of the solvolytic displacement reactions of sulfonate (27).



26

Normally, the reaction gives 2-octanol with 100% inversion of configuration, and there is essentially no difference in rate and stereochemistry in the presence of CTABr. But with NaLS the reaction is strongly inhibited and there is a significant change in stereochemistry, the 2-octanol is produced in this case with 56% (rather than 100%) inversion of configuration. The strong bonding and stereochemical modification observed by Bergman has interesting implications for the long-sought use of micelles in asymmetric induction.

This study is an attempt to synthesize a new class of chiral surfactants with the following formulae and observe the physical properties of their aqueous solutions.



$R = C_{16}H_{33}$, $C_{12}H_{25}$

$R' = CH_3$, C_2H_5

These surfactants may form tightly-packed non-spherical micelles in the presence of NaOH or alkylamine and these micelles, just like enzyme catalysts, may serve as stereoselective templates.

If they act as agents of stereochemical control, this new class of chiral surfactants could be used as inexpensive reusable catalysts for the synthesis of optical active molecules from optical inactive ones. In order to evaluate this stereospecificity, we propose a kinetic study of the reactivity of several chiral reactants, held in these micelles.

Catalysis in Solutions of Long-Chain Macromolecules

Studies of the viscosity and solubilization properties of some poly-4-vinyl-N-alkylpyridinium bromides and chlorides give information on the degree of hydrophobic association in the polymer solutions. Because hydrophobic associations are necessary for catalytic effectiveness of micelles, we will discuss the most important results of these studies.

Fuoss and Strauss[22] have measured the viscosities of solutions containing various concentrations of the poly-

electrolyte made by reacting n-butyl bromide with polyvinylpyridine (average molecular weight 77,000). The reduced viscosities η_{sp}/C, calculated from these data, when plotted against polyelectrolyte concentration, extrapolate to an intrinsic viscosity $[\eta]$ which depends only on the configurations of the polyelectrolyte molecule.

The reduced viscosity of the polyelectrolyte (poly-4-vinyl-N-n-butylpyridinium bromide, C_4PVP) in water is much larger than that of the uncharged polymer (poly-4-vinyl pyridine). This can be explained by the effect of the electrostatic repulsive forces between the ionized pyridinium groups, which would stretch the polymer chain and cause a very large reduced viscosity.

Polyelectrolytes made by reacting long chain alkyl bromides with polyvinylpyridine are known as polysoaps. The length of their alkyl groups may range from ten to twenty methylene groups. Strauss and Jackson[23] prepared the polysoap poly-2-vinyl-N-n-dodecylpyridinium bromide, and determined the viscosity of its aqueous and alcoholic solutions. Their observations are summarized below:

(A) The intrinsic viscosity of the polysoap in water was much smaller than the instrinsic viscosity of the parent polymer (poly-2-vinylpyridine), showing that the polysoap must exist in a relatively compact conformation in water. Strauss explained this by van der Waals attractive forces between the hydrocarbon chains, which are predominant and larger than the

repulsive electrostatic forces between the pyridine groups.

(B) The polysoap acts as a solubilizer. In a comparison between the polysoap and the monosoap (N-n-dodecylpyridinium bromide), at corresponding weight concentrations, isooctane is more soluble in the polysoap solutions than in the monosoap solutions. Strauss assumed that the soap molecules form large and more efficient micelles when they are attached to a polymer chain than when they are free. The polymer hydrocarbon chain may contribute to the solubilization.

In a later study Strauss[24] pointed out that the differences between the polysoap and conventional synthetic polyelectrolytes must be due to the presence of the long hydrophobic side chains in the polysoap molecules. They studied the gradual transition from a typical polyelectrolyte (poly-4-vinyl-N-ethylpyridinium bromide, PEB) to a polysoap (poly-4-vinyl-N-dodecylpyridinium bromide, C_{12}PVP), by selectively quaternizing 6.7, 13.6, 28.5, and 37.9% of the nitrogens of poly-4-vinylpyridine with n-dodecyl bromide and the remainder with ethyl bromide.

The viscosity and solubilization abilities of their aqueous solutions were compared. The reduced viscosity showed a more than hundred-fold over-all decrease, as the proportion of the dodecyl groups in the polysoap molecules increased. The van der Waals attractive force of the dodecyl

groups apparently caused the polysoap molecules to contract to almost protein-like compactness.

They also reported that the best solubilizer for three additives (n-decane, benzene, and 1-heptanol) is the "37.9%" polysoap containing the highest N-dodecyl content. Decane solubilization dropped off extremely rapidly with decreasing dodecyl group content, reaching a value of zero for the "13.6%" polysoap. The solubilization limits of benzene and heptanol decreased by factors of ten and two, respectively, from the "37.9%" to the "13.6%" polysoap. Dilute solutions of the "6.7%" polysoap or the polyelectrolyte (polyvinylethylpyridinium bromide) solubilized neither benzene nor heptanol to any measurable extent. These results clearly indicate that the dodecyl groups are responsible for the solubilization.

Strauss and coworkers[25] also studied the effect of dodecyl group content on solubilization and reduced viscosity of the polyelectrolyte (PEB) and four polysoaps ("6.7%", "13.6%", "28.5%", and "37.9%") in 0.0226 M KBr at 25°C.

Although the "surface" of a polysoap aggregate in solution consists mostly of hydrophilic pyridinium groups, Strauss concluded that beneath the surface is a hydrophobic region which is responsible for the greater solubilizing ability of polysoaps compared to the hydrophilic polyelectrolytes. He further postulated a critical dodecyl group content analogous to the critical micelle concentration (cmc) of ordinary soaps. Polysoaps with a content below

this limit behave like hydrophilic polyelectrolytes with little solubilizing ability, while polysoaps above this limit act like micelles. By studying a series of polysoaps with increasing dodecyl group content, Strauss observed a sudden change in viscosity from polyelectrolyte to polysoap behavior when the dodecyl group content rose above 6.7%.

In an extensive review of polyelectrolyte and micellar catalysis, Morawetz[10] discussed three factors that account for the high catalytic efficiency of some polymers.

(1) The degree of protonation of a basic group when it is attached to a polymer backbone.

To illustrate this effect, Morawetz compared poly-4-vinylpyridine (PVP) and 4-methylpyridine, its low molecular weight analog, which are used as nucleophilic catalysts in the solvolysis of phenyl esters. Spectrophotometric titration data have shown that at pH 2.6 the polymer has 36% of its pyridine residues in the basic form, while in the monofunctional analog only 0.25% of the molecules are present in the form of the conjugate base.

On this basis, Morawetz estimated, that the polymer would be more than 100 times as effective as the monomer analog, in a nucleophilic reaction or when they are used as catalysts for such reactions as the hydrolysis of dinitrophenyl acetate.[26]

(2) Bifunctional catalysis resulting from a cooperative effect of two groups attached to the macromolecules.

Swain and Brown[27] first introduced the concept of bifunctional catalysis which accounts for the unusually large catalytic efficiency of 2-hydroxypyridine in the mutarotation of tetramethylglucose. Since phenol acts as an acid catalyst and pyridine as a base catalyst in that reaction, they concluded that a compound with an acidic hydroxyl and a basic nitrogen at the proper spacing could cause concerted attack with a lower activation energy on the sensitive bond of a reactive molecule.

Copolymers of 4(5)-vinylimidazole with p-vinylphenol were also found to catalyze the hydrolysis of p-nitrophenylacetate.[28] A cooperative attack of phenolate and imidazole residues on the ester group, at higher pH values, appear at least to contribute to the catalytic activity of the polymer.

(3) The concentration of "substrate" molecules in the domain of polymers due to electrostatic interaction or hydrophobic forces.

Morawetz found that at any concentration of the catalytic polyion, the reaction rate approaches a maximum when the charged reagents displace all other counterions in the polymer chain.[29]

The hydrophobic bonding of a substrate to a polymer carrying catalytic groups could enhance the catalysis. A system of this type was obtained by adding p-nitrophenyl laurate to polyethyleneimine partially acylated

with a long chain fatty acid; p-nitrophenol was extremely rapidly released.[30] Morawetz also pointed out that polymers with catalytic groups close to an asymmetric center, should show different rates for stereoisomeric substrates.

The study of catalytic effect in solutions of flexible chain polymers and micelles may provide valuable information concerning the use of synthetic polysoap and micelles as catalysts in organic reaction.

PART II

EXPERIMENTAL PROCEDURES

All melting points were determined with a Thomas-Hoover melting point apparatus, model No. 6404 H. The NMR spectra of all surfactants in this work were recorded on a JOEL MINIMAR-100 Nuclear Magnetic Resonance Spectrophotometer, operating in the external lock mode with a probe temperature of about 30°. The solvent was Deuterium Oxide. No internal reference (such as NaDDS) was used because such compounds are known to affect micellar structure. Chemical shifts are reported in ppm downfield from the C-methyl signal. Optical rotations were measured at the sodium D line with a Perkin Elmer model 50 polarimeter, in ethanol. All compounds employed in this study were stored over $CaCl_2$ until used.

N,N-Dimethyl N-[2-hydroxyethyl] N-dodecylammonium bromide (DDOH, 13)

Bromoethanol (7.09 ml, 0.1 mol) was added to a solution of freshly distilled N,N-dimethyl-dodecylamine (21.3 g, 0.1 mol) in isopropanol (100 ml). The quaternization was carried out at reflux temperatures for 120 hr. The detergent was precipitated with dry ether after evaporation of excess solvent and the product was filtered in the cold and dried in vacuo ($CaCl_2$). A light amber "cement-like" solid was obtained. Recrystallization of the crude product from dry ether absolute alcohol (2:1) followed by drying ($CaCl_2$)

for several months gives 3,5 g (10,6%): mp 156-165°, nmr (D_2O); C-methyl 0.00 ppm, C-methylene 0.44 ppm, N-methyl 2,34 ppm, N-methylene 2,71 ppm, O-methylene 3,19 ppm, D_2O and OH 3.84 ppm.

N,N-Dimethyl N-[2-hydroxyethyl] N-hexadecylammonium bromide (CTOH, 14);

N,N-Dimethyl ethanolamine (8.9 g, 0.1 mol, bp 139) was added to 1-bromohexadecane (30.5 g, 0.1 mol, Aldrich) and 100 ml of isopropanol and the mixture heated at reflux for 10 days. The product was isolated and purified by the method used for 13. A fine hygroscopic white powder (29.8 g, 75.6%) was obtained: mp 175,5-181°; nmr, C-methylene 0.45 ppm, N-methyl 2.37 ppm, N-methylene 2.71 ppm, o-methylene 3.21 ppm, and D_2O-OH 3.94 ppm.

N,N-Dimethyl dl-alanine

DL-alanine (11.5 g, 0.13 mol) and Pd/C (3.1 g, 10%) were suspended in aqueous formaldehyde solution (250 ml, 7,6%) and hydrogenated 16 hr (initial pressure of 26 psi). The Pd/C was removed by filtration through Kieselguhr and the filtrate was evaporated to near dryness on a warm hot plate. Before the mixture was completely dry, water was added and the mixture evaporated again, in order to remove excess formaldehyde. The white solid was dissolved in hot absolute ethanol (200 ml) and the product precipitated upon the addition of acetone. A white crystalline solid (11,1 g, 94.87%, mp 172-177°) was obtained.

N,N-Dimethyl N-dodecylalanine (zwitterion), (23):

N,N-Dimethyl dℓ-alanine (5.34 g, 0.05 mol), 1-bromohexadecane (12.5 g, 0.05 mol, Aldrich) and isopropanol (150 ml) were heated at reflux for 180 hr. The product (7.86 g, 44.2%) was isolated and purified by the method used for 13. The product (mp 95-100°, lit.[31] 108°) had an nmr spectrum consistent with the assigned structure.

N,N-Dimethyl N-[2-hydroxyethyl] N-dodecylammonium chloride (DDOHCl, 27):

Freshly distilled N,N-dimethyl-dodecylamine (21.3 g, 0.1 mol, 150/0.3 mm Hg) and 2-chloroethanol (8.0 g, 0.1 mol) in isopropanol (100 ml) were heated at reflux for 160 hr. The solvent was evaporated in vacuo and the product was precipitated with excess dry ether. Residual solvent was removed from the crude product by filtration in the cold followed by drying under reduced pressure (over $CaCl_2$). A white solid (37.8 g, 57.2%, mp 173.5-181°) was obtained. The product was further purified by recrystallization from ethanol-ether (mp 180-182°); nmr, C-methylene 0.44 ppm, N-methyl 2.34 ppm, N-methylene 2.67 ppm, O-methylene 3.20 ppm, D_2O & OH 3.88 ppm.

N-Methyl N-dodecyl 3-hydroxy-piperidinium bromide (DPBr, 28):

Racemic 3-hydroxy-N-methyl-piperidine (Aldrich) was added to 1-bromododecane (24.9 g, 0.1 mol), and isopropanol

(100 ml). The mixture was heated at reflux for 156 hr. The solvent was removed under reduced pressure on a rotary evaporator to yield a yellow precipitate upon addition of excess dry ether. The crude product (31.2 g, 85.8%) was obtained by filtration in the cold followed by drying in vacuo. The detergent was further purified by recrystallization three times from redistilled acetone to give a hygroscopic white powder (25.5 g, 61%, mp 157-160°) and had an nmr spectrum consistent with the assigned structure.

N-Methyl N-hexadecyl 3-hydroxy-piperidinium bromide (CTPBr, 29):

Compound (29) was prepared by refluxing racemic 3-hydroxy-N-methyl-piperidine (11.5 g, 0.1 mol, yellow viscous liquid) with 1-bromohexadecane (30.6 g, 0.1 mol, bp 144^{2}) in isopropanol (100 ml) for 9 days. The light yellow solution became a clear reddish brown liquid when reaction was complete.

The reaction mixture was divided in two parts:

(1) The solvent was removed in vacuo and the product was precipitated with excess dry ether. The precipitate was filtered and dried under reduced pressure (over $CaCl_2$). Some yellow powder (12.4 g, mp 173.5-178°) was obtained.

(2) The detergent precipitated spontaneously after stirring at room temperature overnight. The product was removed by filtration and dried under reduced pressure (over

$CaCl_2$). Some yellow crystals (19.5 g, mp 161-165°) were obtained.

The combined precipitates were further recrystallized from acetone. The product (26.5 g, 63.1%, mp 176-180.5°) had an nmr spectrum consistent with the assigned structure.

L-2-Dimethylamino-1-butanol:

A mixture of Pd/C (2.5 g, 10%), L-2-amino-1-butanol (Aldrich, 90% optically pure, 35.9 g) and formaldehyde solution (200 ml, 38%) was hydrogenated for 16 hr (initial pressure 35 psi). After the pressure had dropped to 28 psi, the Pd/C was removed by filtration through Kieselguhr. The filtrate was then evaporated on a hot plate with stirring. To the nearly dry residue water was added and evaporated in order to remove formaldehyde. The residue (30 ml), a viscous yellow liquid, was distilled (1-2 mm Hg) through a glass bead column, to give three fractions: (1) 92-97° (3.0 g, n_D^{27} 1.4460); (2) 97-99°, (6.0 g, n_D^{27} 1.4485, $[\alpha]_D$ = -16.3 (5,EtOH)); (3) 95-105° (5.0 g, n_D^{27} 1.4497, $[\alpha]_D$ = -13.8). The middle fraction was colorless but the final fraction was slightly yellow. NMR spectra revealed that fractions (2) and (3) were very nearly identical; all three contained at least 10% of an unidentified impurity.

L-2-N-Hexadecyl N,N-dimethylammonio-1-butanol bromide (30):

L-2-N,N-Dimethylamino-1-butanol (5.7 g, 0.0049 mol,

fraction (2)), 1-bromohexadecane (14.8 g, 0.049 mol), and isopropanol (20 ml) were heated at reflux (96 hr). The resulting coffee colored solution was concentrated in vacuo to a viscous brown liquid (15 g). The nmr spectrum was consistent with the assigned structure but additional peaks indicated the presence of impurities. The liquid did form a water insoluble perchlorate salt which is expected for hydrophobic quaternary ammonium salts. The color of an aqueous solution of (30) changed from brown to tan at high pH (pH > 13) and the viscosity and turbidity of an alkaline solution increased markedly over several days time.

Purification of 4-vinylpyridine:

Aldrich 4-vinylpyridine has a red color due to added phenyl-β-naphthylamine stabilizer. It was distilled (bp 29°, 0.49 mmHg) immediately before use. Even in the refrigerator, distilled vinylpyridine became light yellow within 10 hours.

Poly-4-vinylpyridine (32):

A three-neck round bottom flask (250 ml) equipped with a 500 rpm stirrer, thermometer and reflux condenser was flushed with nitrogen. While a positive nitrogen pressure was maintained, benzoyl peroxide (0.054 g, 2.22×10^{-4} mol) was dissolved in 4-vinylpyridine (25 ml, bp $29^{0.49}$) with vigorous stirring at 45°(4 hr). The resulting light amber viscous liquid was poured into excess toluene (1430 ml) and poly-4-vinylpyridine precipitated slowly overnight and was

removed by filtration. After drying in vacuo, a white cement-like product (1.96 g) was obtained.

The polymerization of 4-vinylpyridine (25 ml, bp $29^{0.49}$) with benzoyl peroxide (0.058 g, 2.39×10^{-4} mol) under the same conditions gave a second batch of white plastic-like product. The poly-4-vinylpyridine was purified by dissolving it in just enough nitromethane and adding this solution dropwise to excess toluene. The drop-shaped pellets of polymer (20 g) were dried in vacuo. Poly-4-vinylpyridine is soluble in nitromethane, pyridine, and methanol. It is insoluble in water, ethyl acetate, and dioxane.

Synthesis of "Polysoap" Poly(4-Vinyl-N-n-dodecylpyridinium bromide):

Poly-4-vinylpyridine (1.6 g) was dissolved in nitromethane (65 ml), and after the slight amount of insoluble gel was removed, n-dodecyl bromide (15 ml, bp 140 [11]) was added. The reaction mixture was heated at reflux for 4 hr between 42-47°C. Most of the nitromethane was removed under reduced pressure on a rotary evaporator and the excess dodecyl bromide was decanted and the white product further dried in vacuo. Purification was attempted as follows: The impure polysoap was dissolved in a 5% solution of a butanone-ethanol mixture (containing just enough ethanol to dissolve the polymer), then poured into excess ethyl acetate at 0°C. The product was dried in vacuo.

The product is amorphous and not soluble in water. The

low yield is probably due to precipitation of starting materials. The literature[24] suggests that the product (polysoap) would be approximately 12% quaternized with a dodecyl bromide after this reaction time.

Viscosity Measurements

The viscosities of detergent solutions containing NaOH and, in some cases, octylamine were measured with a Gilmont (size two) falling drop viscometer. The viscometer was maintained at 32° or 35° with a water jacket adapted from a condenser. The water was circulated with a Lauda K2/R constant temperature water circulator. The viscosity was determined from the equation.

$$\mu = K (D - D_s)t$$

where t = time required for a standardized glass bead to fall through 10 cm of solution.

D = density of the glass bead, 2.53 g/cm^3.

D_s = density of the solution, 0.99 g/cm^3.

K = Viscometer Calibration Constant, found to be 3.02 from measurements on pure water.

The viscometer was calibrated using pure water. Deionized distilled water was used for the preparation of the 0.1 M of detergent and octylamine solutions. The viscosity data for surfactants DDOHCl (27), DPBr (28), CTPBr (29), and CTOH (14) are given in Table XII, XIII, XIV, XV, & XVI, respectively, where C_{NaOH} is the concentration of NaOH, and

t is the average time, and μ is the viscosity.

Critical Micelle Concentrations

The critical micelle concentration values were determined by surface tension measurements.[4] Because of the low critical micelle concentrations of surfactants described in this paper it is preferable to determine the cmc by this method.[1]

All surface tension values were measured at room temperature with a simple Cenco-DuNouy Interfacial Tensiometer. Plots of the surface tension against log C_D, [M]; (where C_D is the detergent concentration) decreased with increasing C_D up to a sharp break at the cmc, and then remained constant up to concentrations several fold greater than the cmc. The surface tension was measured conventionally by the DuNouy ring detachment method. Readings were obtained with the pointer set horizontally in front of the mirror. Each surface tension value is the average of two to five determinations. Deionized distilled water was used for all solutions.

Kinetic Study

The reactions were followed spectrophotometrically (λ = 320 nm) at 39°C using a Beckman Model DB spectrometer with a water-jacketed cell compartment. The reactions were initiated by adding 50 μl of an aqueous substrate stock solution (10^{-3} M) to 2.5 μl of 0.01 M NaOH containing, in some cases, surfactant. The solution was mixed by rapid stirring with a glass rod. The concentration of product

formed at time t was determined by the absorbance A_t at 320 nm and the final concentration from the absorbance A_∞ after complete reaction. Rate constants were determined from the slopes of plots of $\log(A_\infty - A_t)$ vs t(sec); such plots were defined by more than 10 points and were nicely linear for more than three half-lives. The first-order rate constants, $K\psi$, are reported in reciprocal seconds.

The surfactants were hexadecytrimethylammonium bromide (CTABr), N,N-dimethyl-N-2-hydroxyehtyl N-hexadecylammonium bromide (CTOH, 27), and N-methy N-dodecyl 3-hydroxy-piperidinium bromide (DPBr, 28).

PART III

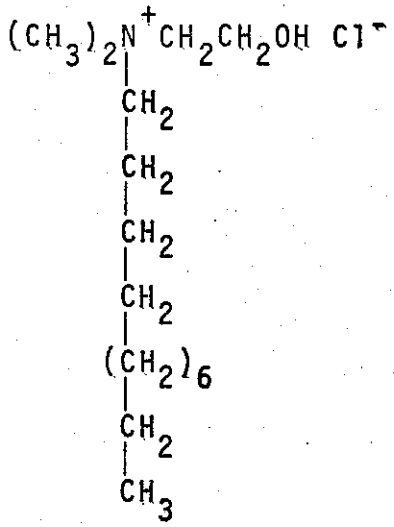
RESULTS AND DISCUSSIONS

All the synthesis work described in this thesis is very similar; in all cases the surfactants were made by quaternizing the appropriate tertiary amine, in isopropyl alcohol. This procedure has been used before,[8] compounds 13, 14, 28, 29, and 30; were made from commercially available tertiary amines. We found that longer reaction times were required to make these detergents than are required for simple quaternizations of tertiary amines not containing OH groups. This suggests that β-OH groups reduce the nucleophilicity of tertiary amines. Isopropanol was generally used for solvent, and anhydrous ethyl ether for recrystallization. Compound 23, was synthesized from DL-alanine [CH_3-CH(NH_2)-COOH] by reductive N-methylation [33,34] followed by quaternization with 1-bromododecane. The surfactant (23) was further purified by recrystallization from acetone. Compound 30 was made by a similar method.

The structure and names of the surfactants used are given in Figure III. Some of these detergents are cationic: N,N-dimethyl N-[2-hydroxyethyl] N-dodecylammonium chloride (DDOHCl, 27), N,N-dimethyl N-[2-hydroxyethyl] N-dodecylammonium bromide (DDOH, 13), N,N-dimethyl N-[2-hydroxyethyl] N-hexadecylammonium bromide (CTOH, 14), N-methy N-dodecyl 3-hydroxy-piperidinium bromide (DPBr, 28), N-methyl N-hexadecyl-3-hydroxy-piperidinium bromide (CTPBr, 29), and

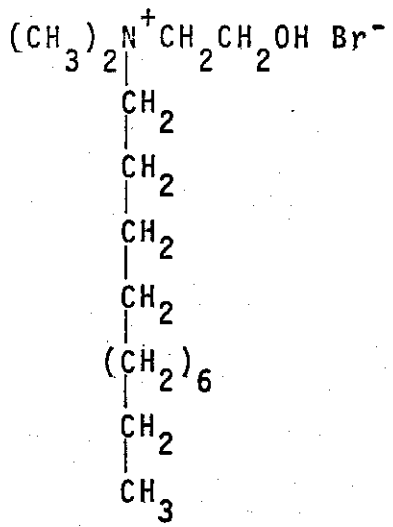
N-hexadecyl ℓ-2-dimethylamino-1-butanol (30); and one is zwitterionic, N,N-dimethyl-N-dodecyl-dl-alanine (23). Their nmr spectra and physical properties are consistent with the assigned structures for most of the compounds.

An attempt to synthesize a polyvinylpyridine polysoap was not completed because of solubility problems. The synthesis of ℓ-2-dimethylamino-1-butanol (30) was not successful because the starting compound was never pure. (It had an impurity that co-distilled.)



DDOHCl (27)

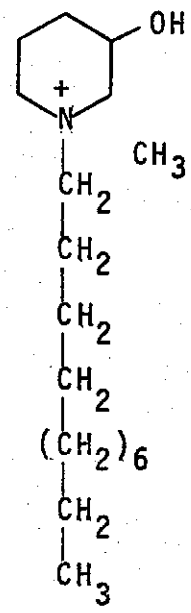
N,N-Dimethyl-N-2-hydroxyethyldodecyl-ammonium chloride



DDOH (13)

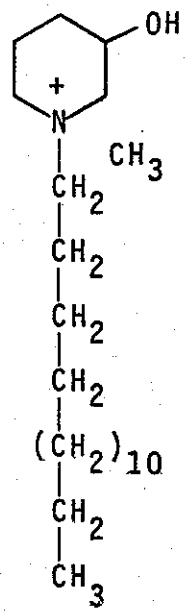
N,N-Dimethyl-N-2-hydroxyethyl dodecyl-ammonium bromide

Figure III Structure of some of the surfactants used.



DPBr (28)

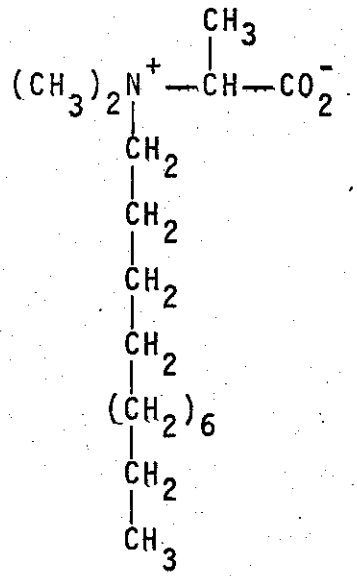
N-methyl N-dodecyl
3-hydroxy-piperidinium
bromide



CTPBr (29)

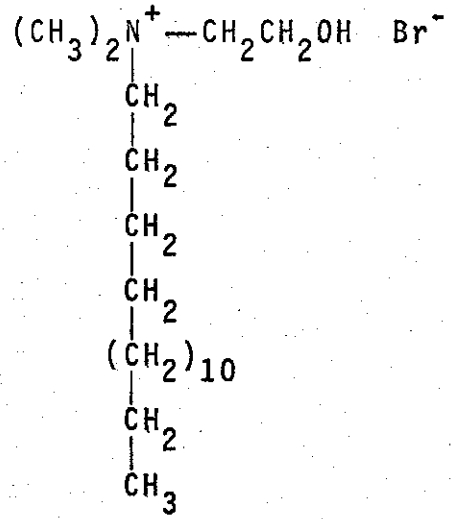
N-methyl N-hexadecyl
3-hydroxy-piperidinium
bromide

Figure III Structure of some of the surfactants used.



(23)

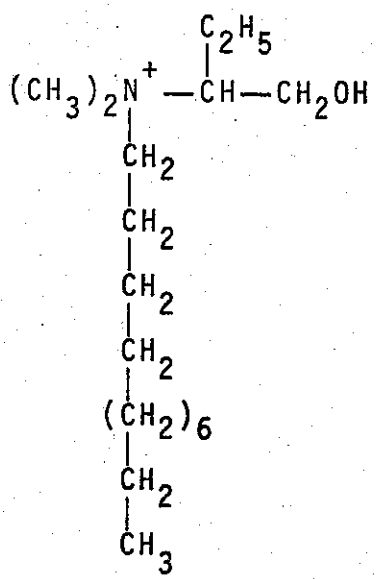
N,N-Dimethyl-N-dodecyl-dl-alanine



CTOH (14)

N,N-Dimethyl-N-2-hydroxyethyl hexadecyl-ammonium bromide

Figure III Structure of some of the surfactants used.



(30)

L-2-N-hexadecyl N,N-
dimethylamino-1-butanol

Figure III Structure of some of the surfactants used.

Determination of Critical Micelle Concentration of Surfactants

In our measurements, one thing which is not often appreciated is that the same experimental data can give different values for the cmc by extrapolation procedures depending on how the data are plotted. Several reasonable extrapolations may give cmc values that differ by as much as 30 percent, which is much more than the error in the surface tension measurements. The mean deviation between duplicate surface tension measurements is two percent or less.

This discrepancy is due to the fact that, these extrapolations involve determining the point of intersection of a curve and a line so that, if different points are chosen as the basis for extrapolation, the cmc estimate is changed. Also, it is clear that different physical properties will give different cmc values.[4] Our cmc measurements agree well with the literature values reported for CTABr (6×10^{-4} M)[4] and for CTOH (as chloride, cmc = 1.2×10^{-3} M).[35] The cmc values of the other compounds have not been reported.

The experimental results for surface tension measurements for various surfactants are given in Tables VI-XI. Plots of surface tension against the logarithm of concentration are given in Figure IV-IX. For comparison, the surface tension obtained for pure water at room temperature was 73.0 dynes/cm. The values of cmc for all the detergents are listed in Table V. The longer the alkyl chain is the lower the cmc.

TABLE V

Detergent	CMC, [M]	% error[a]
DDOHCl (27)	$(2.2 \pm 0.2) \times 10^{-3}$	8
DDOH (13)	$(2.3 \pm 0.1) \times 10^{-3}$	4
CTOH (14)	$(6.8 \pm 1.0) \times 10^{-4}$	15
DPBr (28)	$(1.1 \pm 0.3) \times 10^{-3}$	27
CTPBr (29)	$(7.3 \pm 1.0) \times 10^{-4}$	14
CTABr	$(6.0 \pm 0.5) \times 10^{-4}$	8

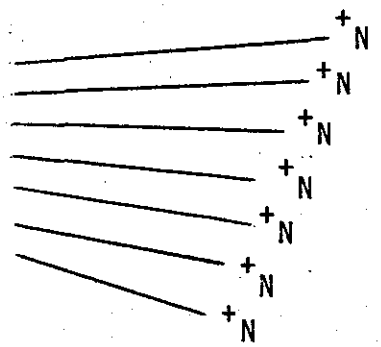
[a] Mean deviation between duplicate CMC measurements.

The viscosity data in Tables XII-XVI show that at low alkali concentrations, there is no increase in viscosity of 0.10 M detergent solutions. In the presence of octylamine, all compounds show a great increase in viscosity. When both octylamine and alkali are added to 0.10 M detergent solutions, all the compounds show a very marked increase in viscosity. Bunton and Ionescu[13] also found that solutions of these surfactants become quite viscous above pH 12.5. We conclude that micelles of 1-hydroxyethyl-2-dimethylalkylammonium bromides (13 & 14, R = n-$C_{12}H_{25}$, n-$C_{16}H_{33}$) are characterized by high intramicellar association when the solutions are highly viscous. The addition of alkali in-

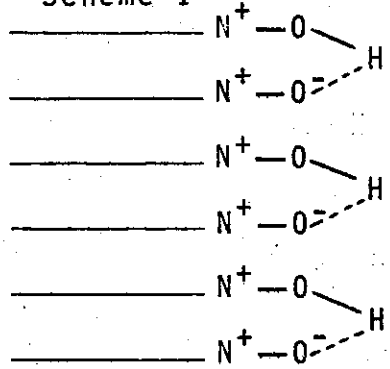
creases the viscosity by allowing a closer association of the cationic head groups, presumably because of zwitterion formation. Bunton and Ionescu estimated pka values of 12.9 and 12.4 for the hydroxyl groups of the dodecyl and hexadecyl surfactants respectively,[13]

$$OH^- + R\text{-}N^+Me_2CH_2CH_2OH \rightleftharpoons R\text{-}N^+Me_2CH_2CH_2O^- + H_2O$$

The electrostatic repulsion between the head groups of 1-hydroxyethyl-2-dimethylalkylammonium ions causes them to repel each other when no base or amine is present, so that the normal shape of micelles is spherical (scheme I). In the presence of NaOH, the cationic head groups of micelles of surfactants ionize to form zwitterions as shown in scheme II, and the shape of micelles will be less spherical.

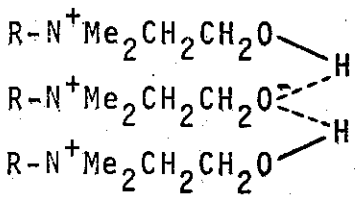


Scheme I



Scheme II

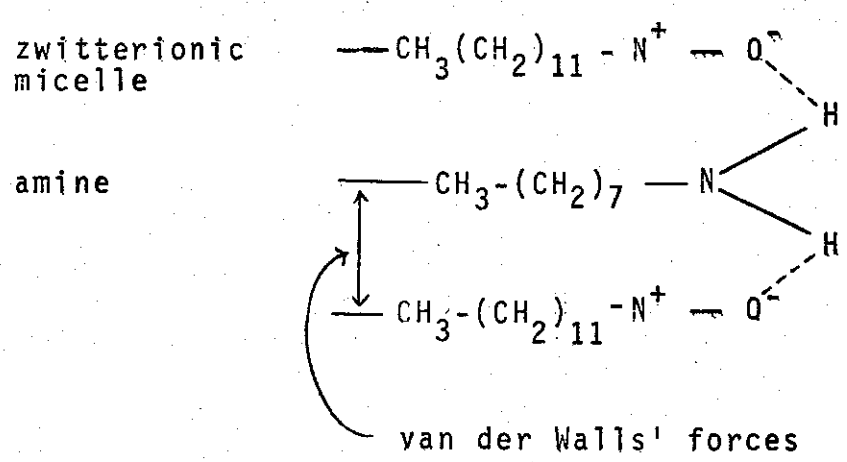
At low alkali concentrations only a few surfactant molecules have been transformed into zwitterions (alkoxide ions) which associate closely with neighboring cationic surfactant molecules. The incorporated alkoxide ions will reduce the usual electrostatic repulsion between cationic head groups and hydrogen bond with unionized hydroxy ethyl groups, both factors favoring intramicellar association. (Scheme III)



Scheme III

At high NaOH concentrations many alkoxide ions are forced together, breaking down the hydrogen bonding pattern. The electrostatic repulsion between adjacent alkoxide ions will thus increase at high NaOH concentrations and cause a slight increase in their average separation.

An added aliphatic amine causes the same viscosity increase, as the data in Tables XII, XIV, XV, and XVI indicate. In the presence of both base and amine, the polar head groups of surfactant micelles are closely associated with amino groups. Amines hydrogen bond with the oxygens of two alkoxide ions at the same time (scheme IV), causing the shape of micelles to become lamellar.



Scheme IV

The increased intra-micellar attraction, is due to van der Walls' forces between the long hydrocarbon chains (the hydrophobic region) of amine and detergent molecules, and hydrogen bonding between alkoxide oxygen atoms and amino protons. Such solutions are very viscous because lamellar structures resist fluid flow more than spherical micelles. Aliphatic alcohols do not cause a viscosity increase when added to alkaline solutions of these detergents, suggesting that simultaneous hydrogen bonding to two surfactant molecules is necessary for "lamellarization".

The nmr spectrum of 0.10 M 27 ($C_{12}H_{25}N^{+}Me_2CH_2CH_2OH,Cl^{-}$; DDOHCl) changes with added NaOH, as shown in Table XVII. The data in Table XVII indicate that added alkali causes a very pronounced broadening of both the N-methyl and C-methylene signals. This broadening is greatest when the alkali concentration is about 0.35, further NaOD making the peaks sharper.

At lower NaOD concentrations, some surfactant micelles are converted into zwitterions. The ionized surfactant molecules reduce the electrostatic repulsive forces between the cationic head groups and hydrogen bond with those neighboring unionized hydroxyethyl groups. This close incorporation leads to higher intra-micellar association and rigid non-spherical micelles. This reduced mobility leads to longer relaxation times and broader peaks in the nmr spectra.

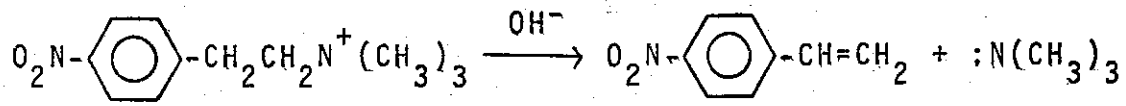
At higher NaOD concentration most surfactant molecules become zwitterions. The reduced spectra broadening observed at high alkali concentration is probably a consequence of the increasedelectrostatic repulsion between the adjacent alkoxide ions reducing intra-micellar association.

The changes in the nmr spectra, and viscosities are all consistent with expected changes in the association of surfactant molecules and their ionization to form zwitterions.

The effect of n-octylamine on the nmr spectrum of CTOH is shown in Table XVIII. The data show that CTOH interacts with amines. The extensive line-broadening means that the motion of CTOH molecules becomes hindered probably because of hydrogen bonding with amine molecules.

We have found that zwitterionic micelles of surfactant ($C_{16}H_{35}N^{+}Me_2CH_2CH_2OH,Br^{-}$, CTOH, 14) are good catalysts for the formation of 4-nitrostyrene and trimethylamine via E_2 elimination of p-nitrophenethyltrimethylammonium iodide. Some attention has been directed toward this reaction by Hughes and Ingold,[36] and more recently by Hodnett, but this

study is the most thorough so far.

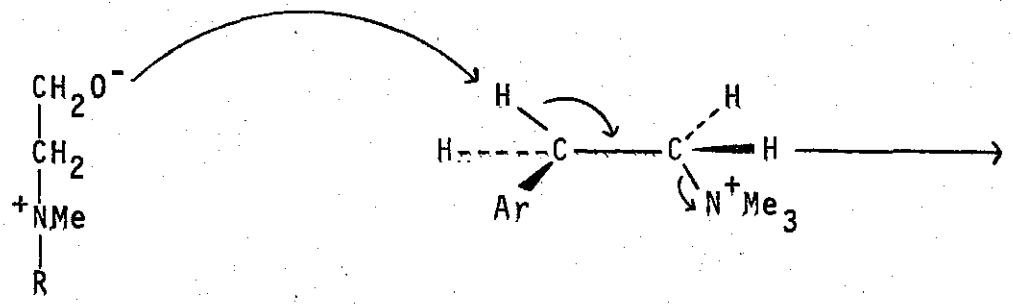


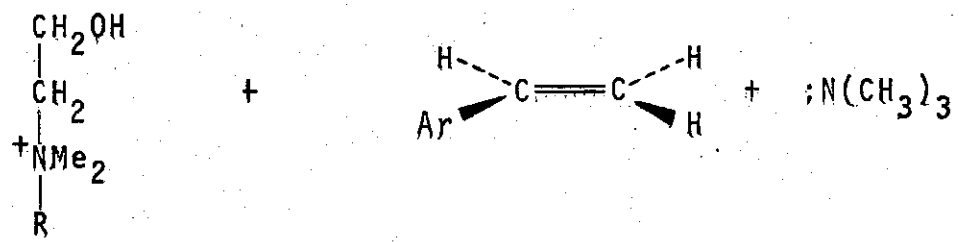
p-nitrophenethyltrimethyl-ammonium iodide

4-nitrostyrene

The first order rate constants, $K\psi$, are plotted against detergent concentration in Figure IV, for the E_2 elimination of p-nitrophenethyltrimethylammonium iodide at 39°C in aqueous solution. In the absence of detergent 10^3 K = 1.23 sec^{-1}.

The rate-enhancement of reaction of p-nitrophenethyltrimethylammonium iodide with hydroxide ion by micelles of surfactants of general structure ($R\text{-}N^+Me_2CH_2CH_2OH$) can be explained in terms of the hydroxy group acting as a general base especially at high pH when it could be ionized (Scheme V).





Another explanation is that hydroxy group of (14) can act as an indirect general base which abstracts a proton from water forming a hydroxide ion which then reacts with substrate. Such a reaction is kinetically indistinguishable from that of the first explanation, but it seems unreasonable. Water is less reactive than hydroxide ion toward p-nitrophenethyltrimethylammonium iodide, and general base catalysis is not of major importance in this E_2 elimination,[36] although it has been observed in some cases.

The first-order rate constants, $k\psi$, for reactions of p-nitrophenethyltrimethylammonium iodide with hydroxide ion in the presence of N-methy N-dodecyl 3-hydroxy piperidinium bromide are given in Figure X, together with earlier results for cetyltrimethylammonium bromide (CTABr), and results for this elimination in the presence of surfactant 14 (CTOH).

The data in Tables XV and XVI show that DPBr is a better catalyst than CTOH in the E_2 elimination, probably because it is more hydrophobic. Our sample of DPBr is a diastereomeric mixture and its catalytic effectiveness may be different from micelles of the purified isomers however its high activity suggests that these isomers may induce chirality, if Moss' conclusion[18] that stereospecificity increases with catalytic activity is correct.

In order to see if chiral surfactants can induce product chirality, we plan to synthesize DPBr from resolved 3-hydroxypiperidine and to separate its diastereomeric isomers by chromatography on an anionic column. The catalytic

effect of purified chiral surfactants on chiral reactants and the stereochemistry and optical purity of several stereoisomeric products in the presence of surfactants will then be determined.

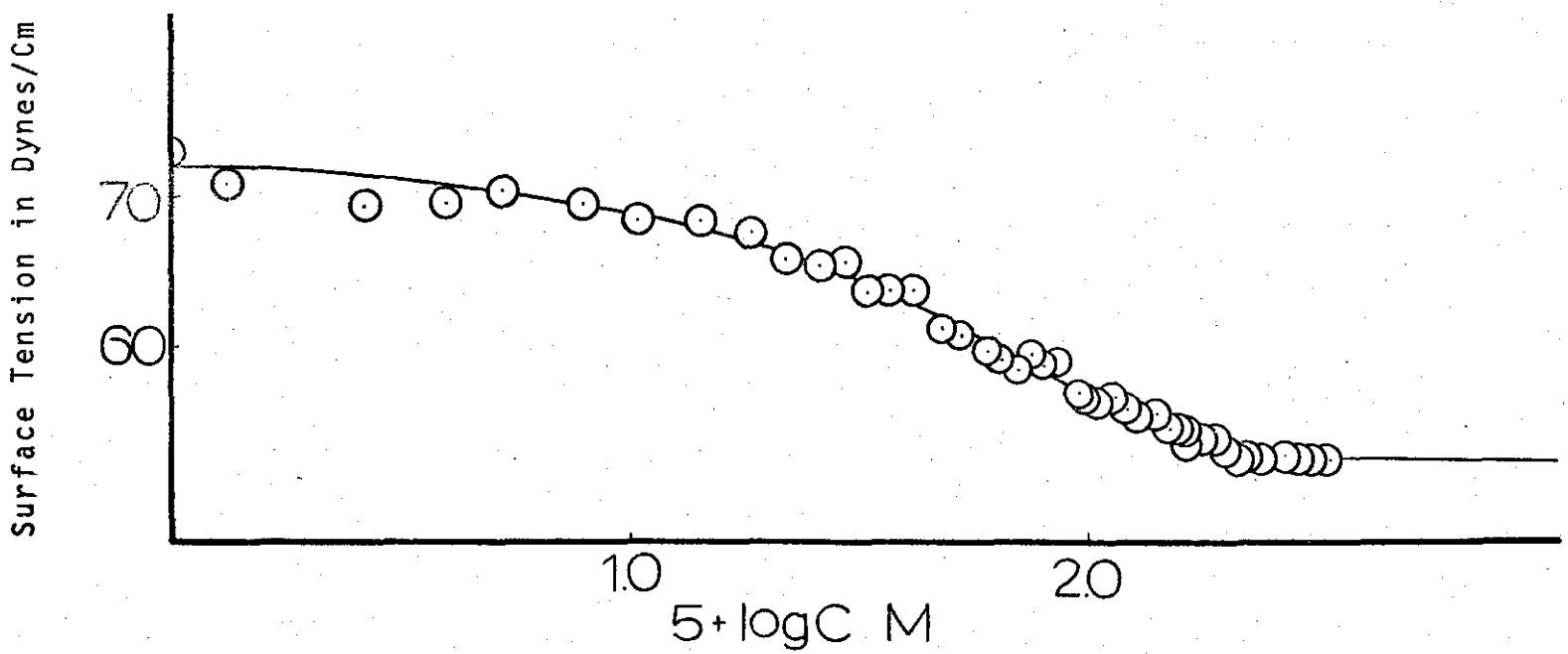


Figure IV Plots of the Surface Tension against (5 + log C) for N,N-Dimethyl N-[2-hydroxyethyl] N-dodecylammonium chloride (DDOHCl, 27).

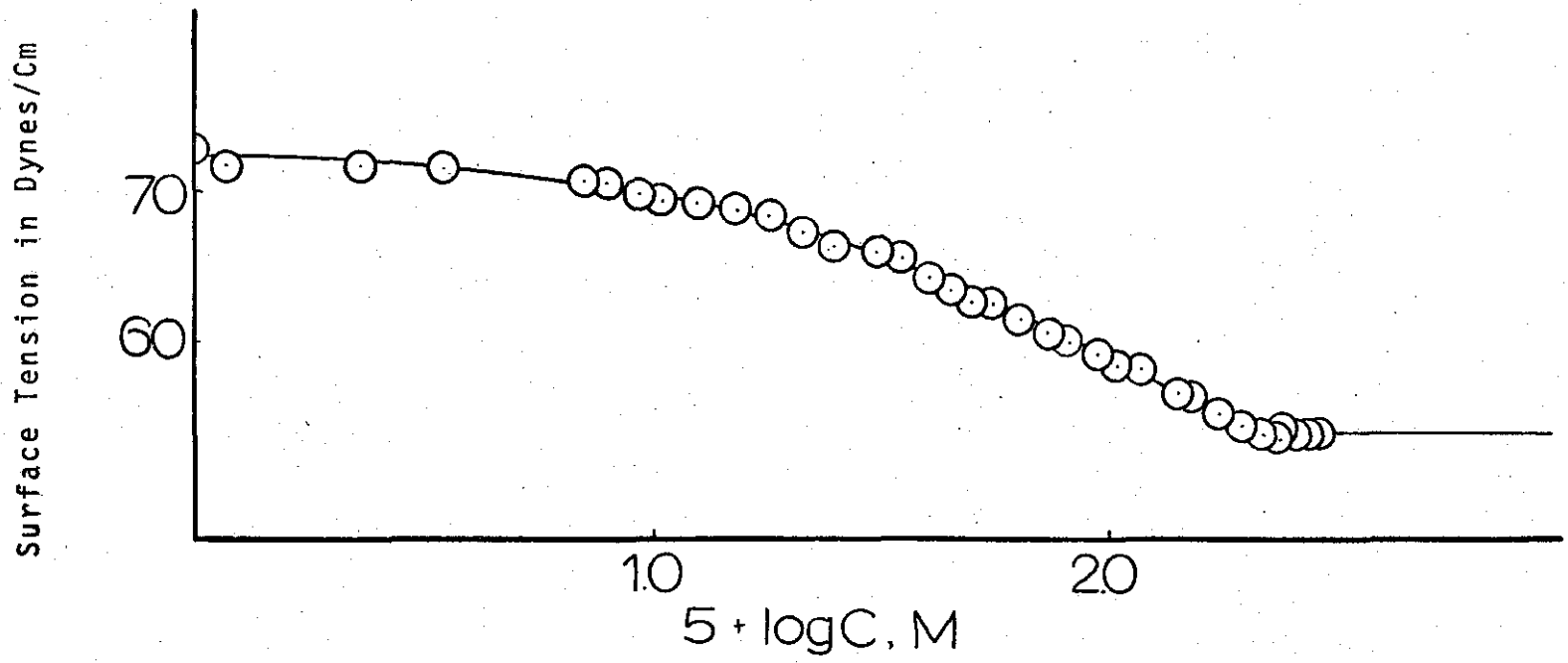


Figure V Plots of the Surface Tension against (5 + log C) for N,N-Dimethyl-N-[2-hydroxyethyl] N-dodecylammonium bromide (DDOH, 13).

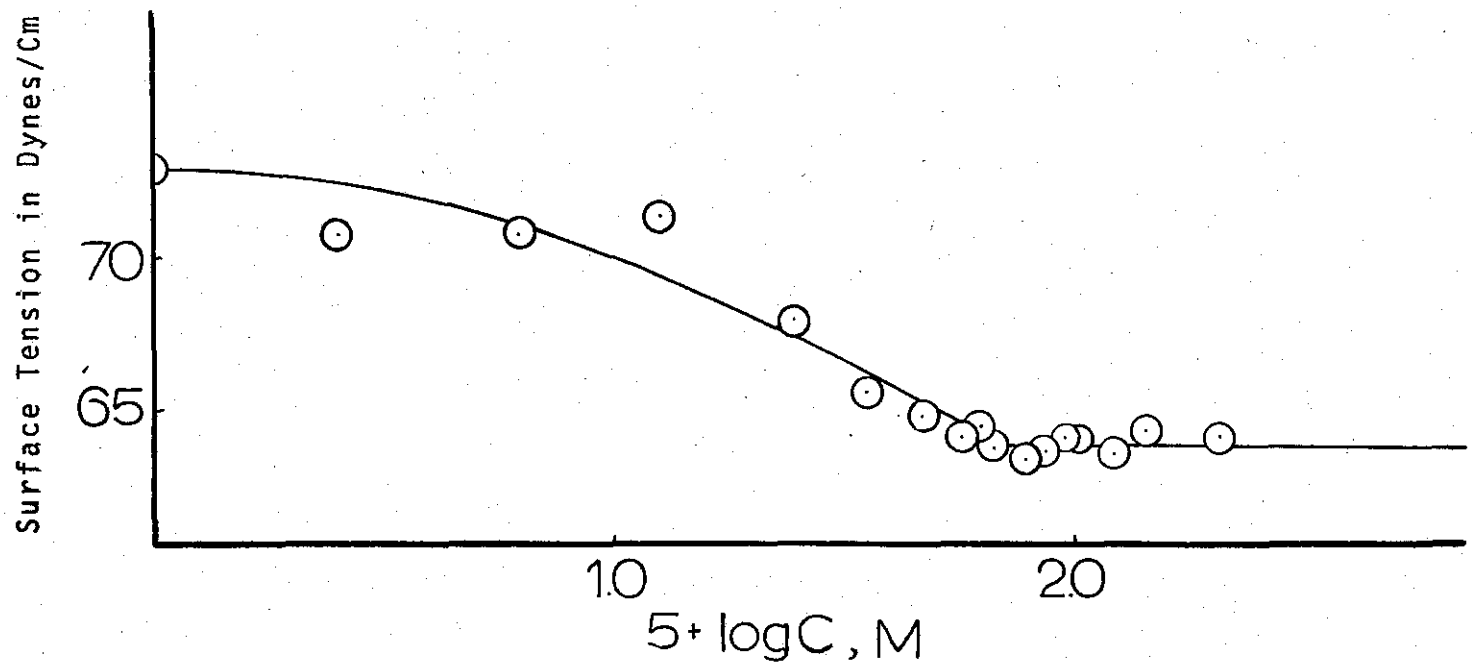


Figure VI Plots of the Surface Tension against (5 + log C) for N,N-Dimethyl N-[2-hydroxyethyl] N-hexadecylammonium bromide (CTOH, $\underset{\sim\sim}{14}$).

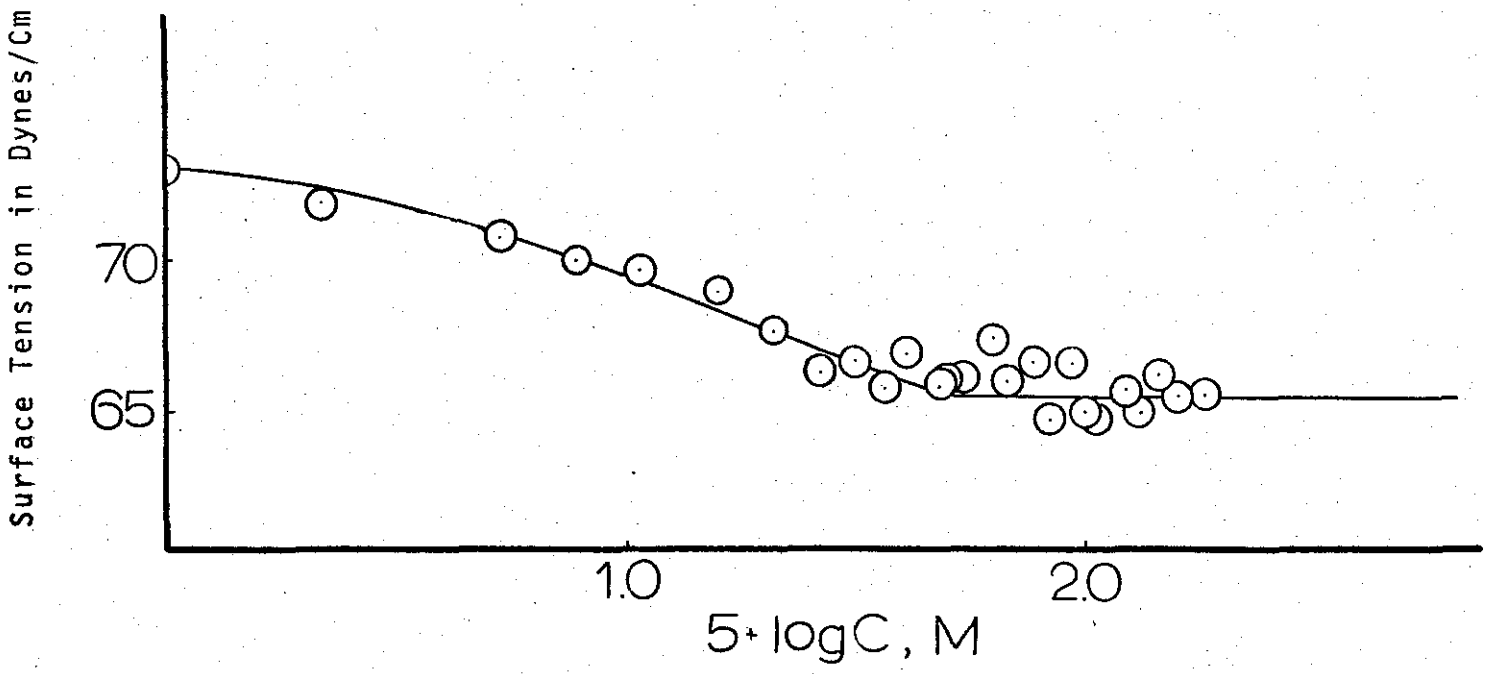


Figure VII Plots of the Surface Tension against (5 + log C) for N-Methyl N-dodecyl 3-hydroxy-piperidinium bromide (DPBr, 28).

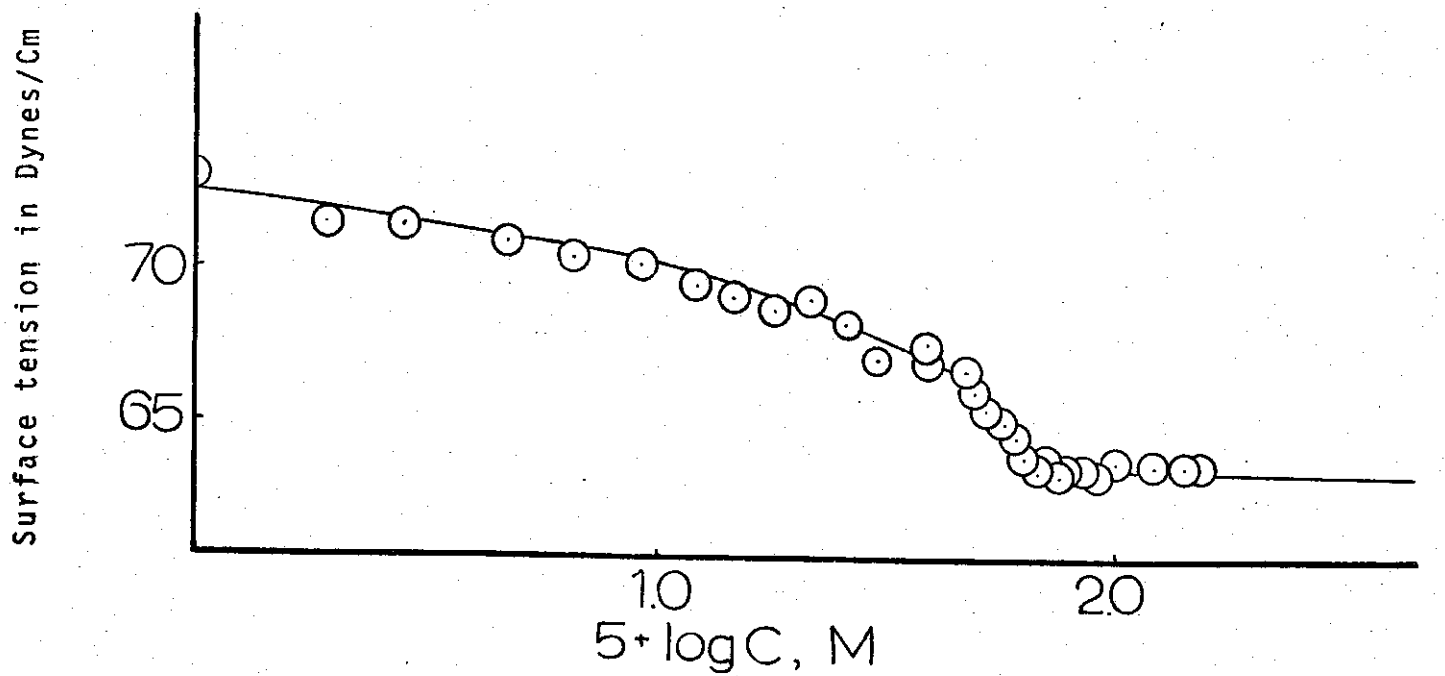


Figure VIII Plots of the Surface Tension against (5 + log C) for N-Methyl N-hexadecyl 3-hydroxy-piperidium bromide (CTPBr, 29).

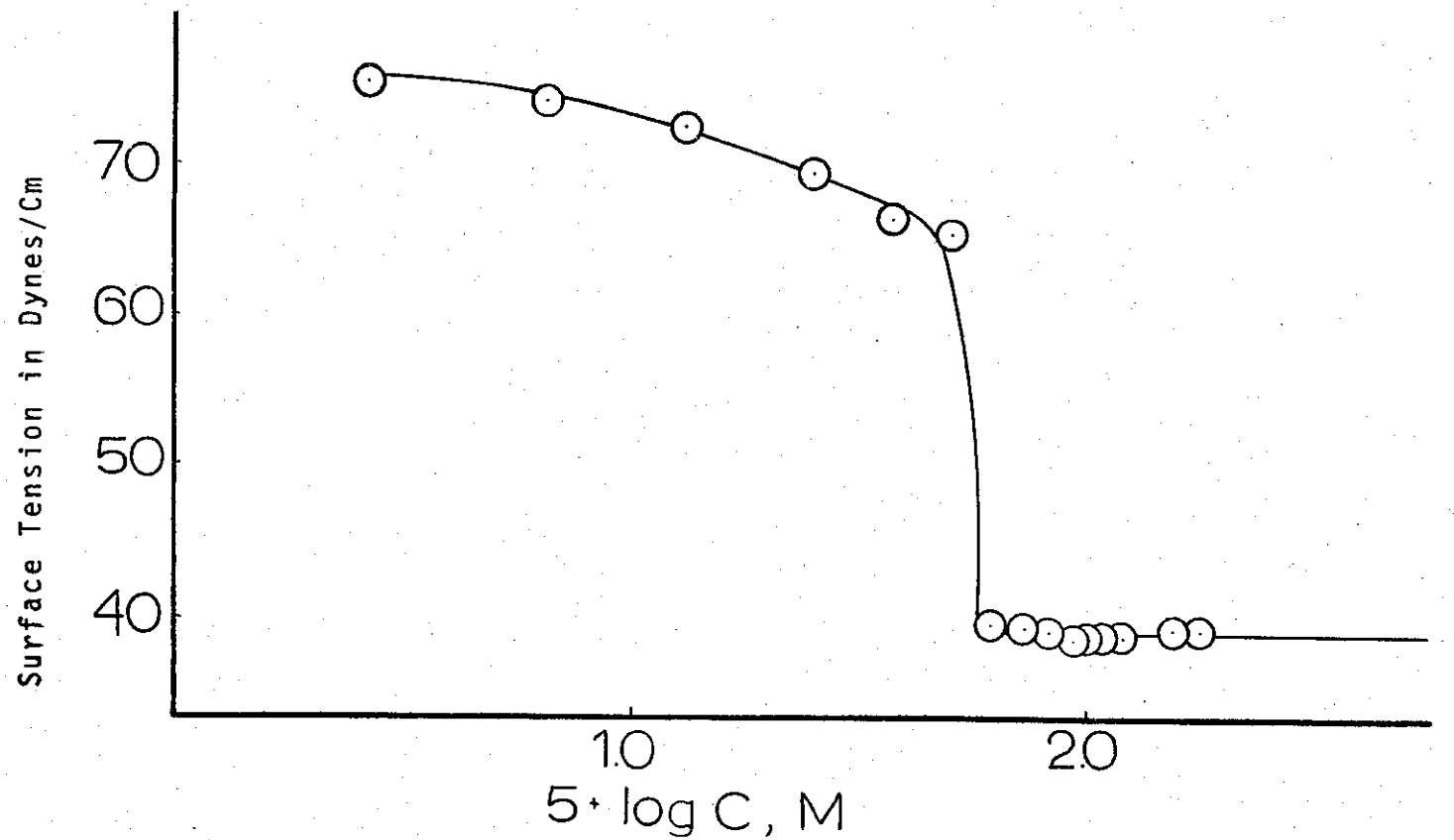


Figure IX Plots of the Surface Tension against (5 + log C) for Hexadetrimethylammonium bromide (CTABr).

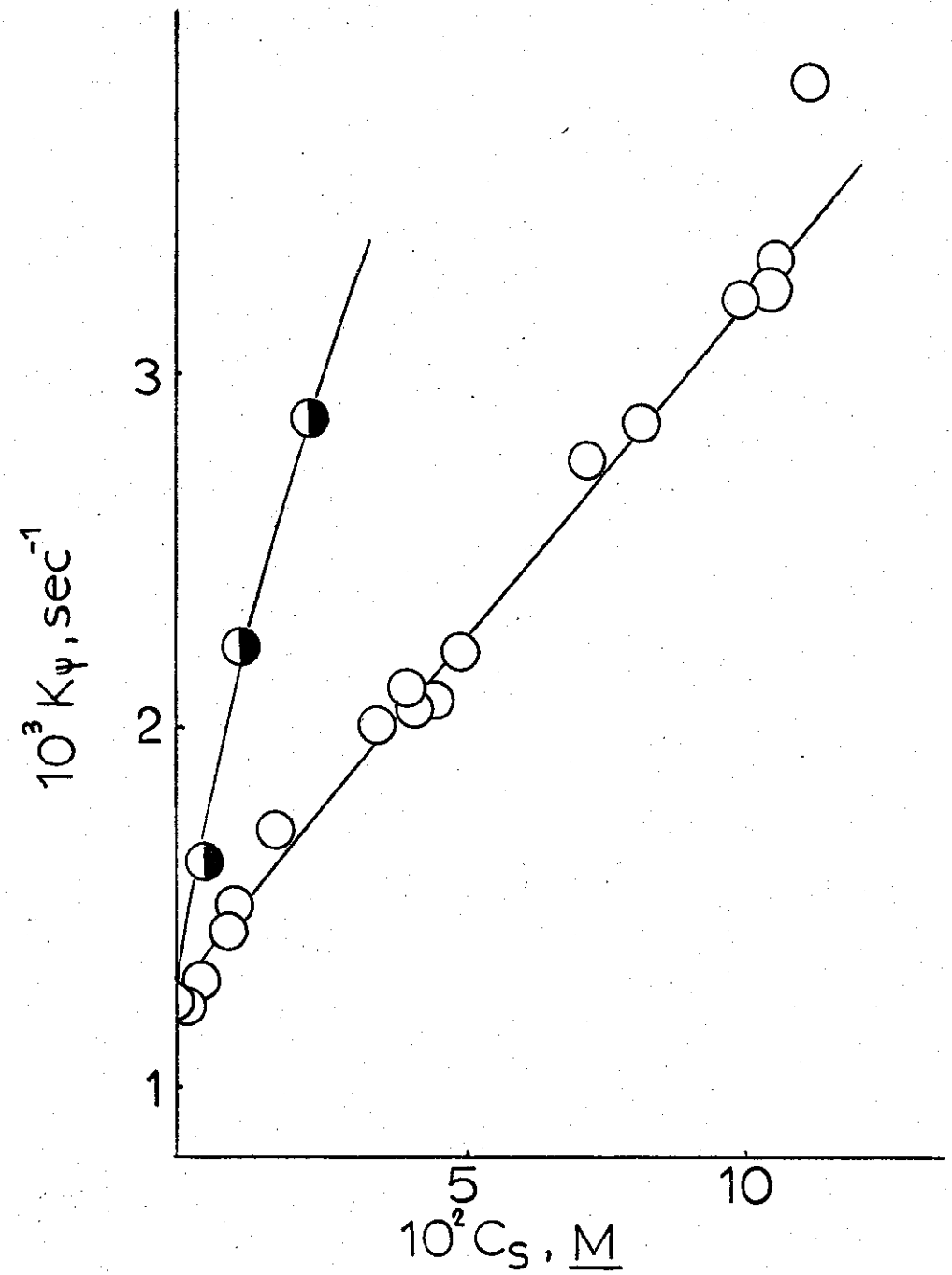


Figure X The observed first-order rate constant K for 4-nitrostyrene formation from p-nitrophenethyltrimethyammonium iodide in 0.1 M NaOH at 39°C, as a function of surfactant concentration, C_s. The surfactants are ○ CTOH (14), and ◑ DPBr (28).

Table VI

Surface Tension Measurements of Aqueous N,N-Dimethyl N-[2-hydroxyethyl] N-dodecylammonium chloride (DDOHCl, 27)[a]

Concentration C_{DDOHCl}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
1.36×10^{-5}	0.1335	70.9
2.71×10^{-5}	0.4330	70.3
4.06×10^{-5}	0.6085	69.7
5.40×10^{-5}	0.7324	70.2
8.07×10^{-5}	0.9069	69.4
1.07×10^{-4}	1.0294	68.4
1.46×10^{-4}	1.1644	68.4
1.85×10^{-4}	1.2672	67.4
2.24×10^{-4}	1.3502	65.9
2.62×10^{-4}	1.4183	65.1
2.99×10^{-4}	1.4757	65.6
3.37×10^{-4}	1.5276	63.7
3.73×10^{-4}	1.5717	63.7
4.21×10^{-4}	1.6243	63.6
4.81×10^{-4}	1.6821	61.0
5.39×10^{-4}	1.7316	61.8
5.96×10^{-4}	1.7752	59.8
6.52×10^{-4}	1.8142	59.1
7.07×10^{-4}	1.8494	58.4

Table VI (Cont.)

Concentration C_{DDOHCl}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
7.67×10^{-4}	1.8848	59.2
8.16×10^{-4}	1.9117	58.9
8.67×10^{-4}	1.9380	58.9
9.48×10^{-4}	1.9768	56.9
9.98×10^{-4}	1.9991	56.7
1.05×10^{-3}	2.0212	56.2
1.14×10^{-3}	2.0569	56.4
1.24×10^{-3}	2.0934	55.9
1.33×10^{-3}	2.1239	55.1
1.41×10^{-3}	2.1492	55.4
1.50×10^{-3}	2.1761	54.5
1.58×10^{-3}	2.1987	54.8
1.66×10^{-3}	2.2201	54.4
1.71×10^{-3}	2.2330	53.6
1.84×10^{-3}	2.2648	53.8
1.95×10^{-3}	2.2900	53.9
2.05×10^{-3}	2.3118	53.1
2.19×10^{-3}	2.3404	52.5
2.30×10^{-3}	2.3617	52.7
2.48×10^{-3}	2.3945	52.5
2.73×10^{-3}	2.4362	52.6

Table VI (Cont.)

Concentration C_{DDOHCl}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
2.96×10^{-3}	2.4713	52.2
3.02×10^{-3}	2.4829	52.5
3.22×10^{-3}	2.5079	52.6
3.37×10^{-3}	2.5276	52.6

[a] In distilled deionized water at room temperature

DDOHCl = $C_{12}H_{25}N^{+}Me_2CH_2CH_2OH,Cl^{-}$.

[b] Average of two determinations.

Table VII

Surface Tension Measurements of Aqueous N,N-Dimethyl N-[2-hydroxyethyl]N-dodecylammonium bromide (DDOH,13)[a]

Concentration C_{DDOH}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
1.18×10^{-5}	0.0719	71.9
2.35×10^{-5}	0.3711	71.8
3.52×10^{-5}	0.5465	71.8
7.01×10^{-5}	0.8457	70.8
8.16×10^{-5}	0.9117	70.6
9.31×10^{-5}	0.9689	69.9
1.05×10^{-4}	1.0212	69.6
1.27×10^{-4}	1.1038	69.1
1.50×10^{-4}	1.1761	68.9
1.84×10^{-4}	1.2648	68.4
2.16×10^{-4}	1.3345	67.3
2.49×10^{-4}	1.3962	66.4
3.13×10^{-4}	1.4955	66.0
3.55×10^{-4}	1.5502	65.8
4.07×10^{-4}	1.6096	64.4
4.58×10^{-4}	1.6609	63.6
5.08×10^{-4}	1.7059	62.8
5.57×10^{-4}	1.7459	62.8
6.52×10^{-4}	1.8142	61.3

Table VII (Cont.)

Concentration C_{DDOH}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
7.44×10^{-4}	1.8716	60.6
8.33×10^{-4}	1.9206	60.1
9.60×10^{-4}	1.9823	59.3
1.08×10^{-3}	2.0334	58.6
1.20×10^{-3}	2.0792	58.2
1.45×10^{-3}	2.1614	56.8
1.55×10^{-3}	2.1903	56.7
1.76×10^{-3}	2.2455	55.3
2.06×10^{-3}	2.3139	54.6
2.20×10^{-3}	2.3424	54.0
2.34×10^{-3}	2.3692	53.9
2.46×10^{-3}	2.3909	54.1
2.65×10^{-3}	2.4232	54.0
2.72×10^{-3}	2.4346	53.9
2.82×10^{-3}	2.4502	54.0
2.92×10^{-3}	2.4654	54.1

[a] In distilled deionized water at room temperature

DDOH = $C_{12}H_{25}N^{+}Me_2CH_2CH_2OH,Br^{-}$.

[b] Average of two to four determinations.

Table VIII

Surface Tension Measurements of Aqueous N,N-Dimethyl N-[2-hydroxyethyl]N-hexadecylammonium bromide (CTOH,14)[a]

Concentration C_{CTOH}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
2.52×10^{-5}	0.401	70.7
6.25×10^{-5}	0.796	70.8
1.24×10^{-4}	1.093	71.3
2.43×10^{-4}	1.386	67.9
3.58×10^{-4}	1.554	65.5
4.68×10^{-4}	1.670	64.8
5.74×10^{-4}	1.759	64.1
6.26×10^{-4}	1.797	64.3
6.77×10^{-4}	1.831	63.7
7.76×10^{-4}	1.890	63.3
8.72×10^{-4}	1.940	63.6
9.64×10^{-4}	1.984	64.0
1.05×10^{-3}	2.021	63.9
1.22×10^{-3}	2.086	63.5
1.46×10^{-3}	2.164	64.2
2.11×10^{-3}	2.322	64.0

[a] In distilled deionized water at room temperature, CTOH = $C_{16}H_{33}N^{+}(CH_3)_2CH_2CH_2OH,Br^{-}$.

[b] Average of three to five determinations.

Table IX

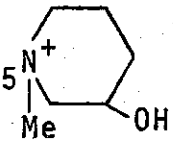
Surface Tension Measurements of Aqueous N-methyl N-dodecyl 3-hydroxy-piperidinium bromide (DPBr, 28)[a]

Concentration C_{DPBr}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
2.19×10^{-5}	0.3404	71.9
5.43×10^{-5}	0.7348	70.8
7.57×10^{-5}	0.8791	70.0
1.08×10^{-4}	1.0334	69.7
1.60×10^{-4}	1.2051	69.0
2.11×10^{-4}	1.3243	67.7
2.61×10^{-4}	1.4166	66.4
3.11×10^{-4}	1.4928	66.7
3.59×10^{-4}	1.5551	65.0
4.07×10^{-4}	1.6096	67.0
4.81×10^{-4}	1.6821	65.9
4.99×10^{-4}	1.6981	66.1
5.44×10^{-4}	1.7356	66.2
6.31×10^{-4}	1.8000	67.4
7.57×10^{-4}	1.8791	66.7
8.37×10^{-4}	1.9227	64.8
9.15×10^{-4}	1.9614	66.7
9.89×10^{-4}	1.9952	65.0
1.06×10^{-3}	2.0253	64.9

Table IX (Cont.)

Concentration C_{DPBr}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
1.20×10^{-3}	2.0792	65.7
1.33×10^{-3}	2.1239	65.1
1.45×10^{-3}	2.1614	66.2
1.57×10^{-3}	2.1959	65.5
1.83×10^{-3}	2.2625	65.7

[a] Indistilled deionized water at room temperature.

DPBr = $C_{12}H_{25}$  ,Br^-.

[b] Average of four to six determinations.

Table X

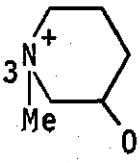
Surface Tension Measurements of Aqueous N-methyl N-hexadecyl 3-hydroxy-piperidinium bromide (CTPBr, 29)[a]

Concentration C_{CTPBr}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
9.49×10^{-6}	-1 + 0.9773	71.5
1.89×10^{-5}	0.2765	71.4
2.84×10^{-5}	0.4533	71.3
4.71×10^{-5}	0.6730	70.8
6.57×10^{-5}	0.8176	70.3
9.32×10^{-5}	0.9694	70.1
1.20×10^{-4}	1.0792	69.5
1.47×10^{-4}	1.1673	69.6
1.83×10^{-4}	1.2625	68.7
2.18×10^{-4}	1.3385	69.0
2.61×10^{-4}	1.4166	68.2
3.03×10^{-4}	1.4814	67.1
3.85×10^{-4}	1.5855	67.4
4.02×10^{-4}	1.6042	66.9
4.64×10^{-4}	1.6665	66.6
5.02×10^{-4}	1.7007	66.0
5.40×10^{-4}	1.7324	65.3
5.77×10^{-4}	1.7612	65.0
6.13×10^{-4}	1.7875	64.5

Table X (Cont.)

Concentration C_{CTPBr}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
6.49×10^{-4}	1.8122	63.8
6.84×10^{-4}	1.8351	63.4
7.19×10^{-4}	1.8567	63.7
7.53×10^{-4}	1.8768	63.2
8.06×10^{-4}	1.9063	63.4
8.70×10^{-4}	1.9395	63.3
9.33×10^{-4}	1.9699	63.2
1.06×10^{-3}	2.0253	63.7
1.22×10^{-3}	2.0864	63.5
1.46×10^{-3}	2.1644	63.5
1.57×10^{-3}	2.1959	63.6

[a] In distilled deionized water at room temperature

CTPBr = $C_{16}H_{33}$  ,Br^-.

[b] Average of four to six determinations.

Table XI

Surface Tension Measurements of Aqueous cetyltrimethy-ammonium bromide (CTABr)[a]

Concentration C_{CTABr}, [M]	5 + log C, [M]	Surface Tension[b] σ [dynes/cm]
2.67×10^{-5}	0.427	75.5
6.64×10^{-5}	0.822	74.2
1.31×10^{-4}	1.117	72.4
2.58×10^{-4}	1.412	69.3
3.79×10^{-4}	1.579	66.6
4.96×10^{-4}	1.700	65.4
6.09×10^{-4}	1.785	39.4
7.18×10^{-4}	1.856	39.3
8.23×10^{-4}	1.915	39.2
9.24×10^{-4}	1.966	38.6
1.02×10^{-3}	2.009	38.8
1.11×10^{-3}	2.045	38.8
1.19×10^{-3}	2.076	39.0
1.54×10^{-3}	2.188	39.1
1.91×10^{-3}	2.281	39.1

[a] In distilled deionized water at room temperature, CTABr = $C_{16}H_{33}N^{+}(CH_3)_3,Br^{-}$.

[b] Average of four determinations.

Table XII

Viscosity of 0.01M DDDOHCl[a] at 37.5°C

$C_{Octylamine}$, M	C_{NaOH}, M	t, sec	η, Viscosity[b], dyne x sec/cm^2
0.00	0.00	10.35	0.80
0.00	0.05	10.05	0.78
0.00	0.10	10.00	0.78
0.02	0.00	10.40	0.81
0.08	0.00	11.40	0.88
0.10	0.00	11.50	0.89
0.02	0.08	10.30	0.80
0.05	0.05	10.60	0.82
0.08	0.02	10.70	0.83
0.10	0.10	12.7	0.98

[a] DDOHCl = $C_{12}H_{25}N^{+}Me_2CH_2CH_2OH,Cl^{-}$.

[b] Average of two determinations.

Table XIII

Viscosity of 0.10M DDOHCl[a] at 32°C

$C_{Octylamine}$, M	C_{NaOH}, M	t, sec	η, Viscosity[b], dyne x sec/cm^2
0.10	0.00	27.60	2.14
0.05	0.10	200.10	15.51
0.00	0.20	408.00	31.62

[a] DDOHCl = $C_{12}H_{25}N^{+}Me_2CH_2CH_2OH,Cl^{-}$.

[b] Average of two determinations.

Table XIV

Viscosity of 0.1M CTOH[a] at 35°C

$C_{Octylamine}$, M	C_{NaOH}, M	t, sec	η, Viscosity[b], dyne x sec/cm^2
0.00	0.00	12.25	0.95
0.00	0.05	10.07	0.83
0.00	0.10	11.30	0.88
0.02	0.00	12.20	0.95
0.08	0.00	28.40	2.10
0.10	0.00	66.25	5.13
0.02	0.08	18.80	1.46
0.05	0.05	201.60	15.62
0.08	0.02	313.90	24.33
0.10	0.10	677.70	52.52

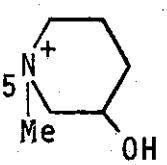
[a] CTOH = $C_{16}H_{33}N^{+}(CH_3)_2CH_2CH_2OH,Br^{-}$.

[b] Average of two determinations.

Table XV

Viscosity of 0.1M CTOH[a] at 35°C

$C_{Octylamine}$, M	C_{NaOH}, M	t, sec	η, Viscosity[b], dyne x sec/cm^2
0.00	0.00	10.80	0.84
0.00	0.05	10.90	0.85
0.00	0.10	10.90	0.85
0.02	0.00	11.00	0.85
0.05	0.00	14.00	1.09
0.08	0.00	22.00	1.71
0.10	0.00	37.00	2.87
0.02	0.08	11.00	0.85
0.05	0.05	20.00	1.55
0.08	0.02	30.00	2.33
0.10	0.10	277.00	21.47

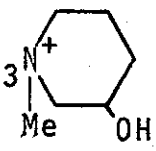
[a] DDPBr =  , Br^-.

[b] Average of two determinations.

Table XVI

Viscosity of 0.10M CTPBr[a] at 35.5°C

$C_{Octylamine}$, M	C_{NaOH}, M	t, sec	n, Viscosity[b], dyne x sec/cm^2
0.00	0.00	11.10	0.86
0.00	0.05	11.10	0.86
0.00	0.10	10.40	0.81
0.03	0.00	14.50	1.12
0.07	0.00	47.50	3.68
0.10	0.00	166.30	12.89
0.02	0.08	50.10	3.88
0.05	0.05	234.70	18.19
0.08	0.02	c	c
0.10	0.10	328.00	25.42

[a] CTPBr = $C_{16}H_{33}$  , Br^-.

[b] Average of two determinations.

[c] Too viscous to measure.

Table XVII

Effect of NaOH on the NMR Spectrum of DDOHCl[a]

$10^2\ C_{NaOH}$,	$10\ W_{\frac{1}{2}}^{C-CH_2}$,
M	PPM[b]
0.00	10.50
0.05	17.00
0.10	24.00
0.15	26.00
0.20	27.50
0.25	24.00
0.30	25.00
0.35	35.50
0.40	34.00
0.45	19.50
0.50	13.50

[a] For 0.10M DDOHCl = $C_{12}H_{25}N^{+}Me_2CH_2CH_2OH,Cl^{-}$ in D_2O at room temperature.

[b] $W_{\frac{1}{2}}$ = Peak width at half-height for C-methylene signals and N-methylene of DDOHCl(27) respectively.

Table XVIII

Effect of n-octylamine on the NMR Spectrum of CTOH[a]

$10^2 C_{amine}$[b],	$\delta^{C\text{-}Me}_{N\text{-}Me_2}$[c],	$W_{\frac{1}{2}}^{NMe_2}$,
M	PPm	Hz
0.00	2.36	2.90
0.89	2.34	2.70
1.77	2.35	3.60
2.66	2.37	3.90
4.03	2.34	8.80
4.84	2.31	9.60
7.10	2.29	12.00

[a] For 0.10 M CTOH in D_2O [b] concentration of n-octylamine chemical shift of the N-methyl proton signal of CTOH, measured downfield from the C-methyl proton signal.

[c] Width at half-height of N-methyl proton signal.

Table XIX

Effect of CTOH on the rate of p-nitrostyrene formation from p-nitrophenethyltrimethylammonium iodide[a].

$10^2 C_{CTOH}$[b], M	$10^3 k_{Obs}$[c], sec^{-1}
0.00	1.23
0.25	1.23
0.50	1.29
0.90	1.43
1.05	1.52
1.81	1.72
3.63	2.04
4.10	2.11
4.20	2.06
4.78	2.06
5.03	2.24
7.26	2.74
8.25	2.85
10.00	3.20
10.60	3.21
10.60	3.32
11.40	3.80

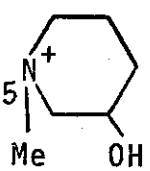
[a] For 0.10M NaOH at 39°C; [b] CTOH concentration; CTOH = $C_{16}H_{33}N(CH_3)_2CH_2CH_2OH,Br^-$; [c] observed first-order rate constant.

Table XX

Effect of DPBr on the rate of p-nitrostyrene formation from p-nitrophenethyltrimethylammonium iodide[a].

$10^2 C_{DPBr}$[b], M	$10^3 k_{Obs}$[c], sec^{-1}
0.00	1.23
0.59	1.63
1.18	2.22
2.36	2.87

[a] For 0.10M NaOH at 39°C; [b] DPBr concentration,

DPBr = racemic $C_{12}H_{25}$ 

, Br^-; [c] observed first-order rate constant.

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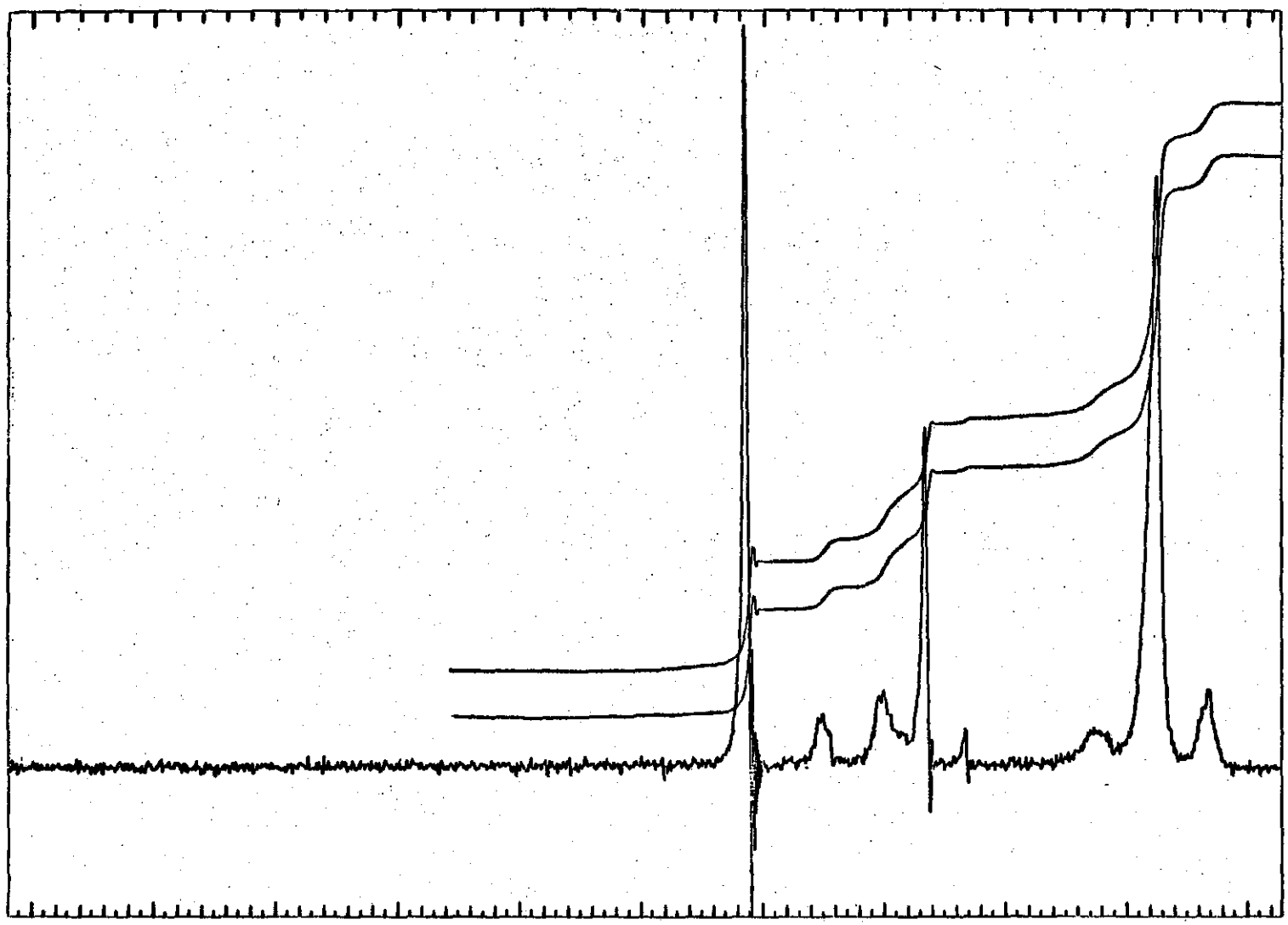
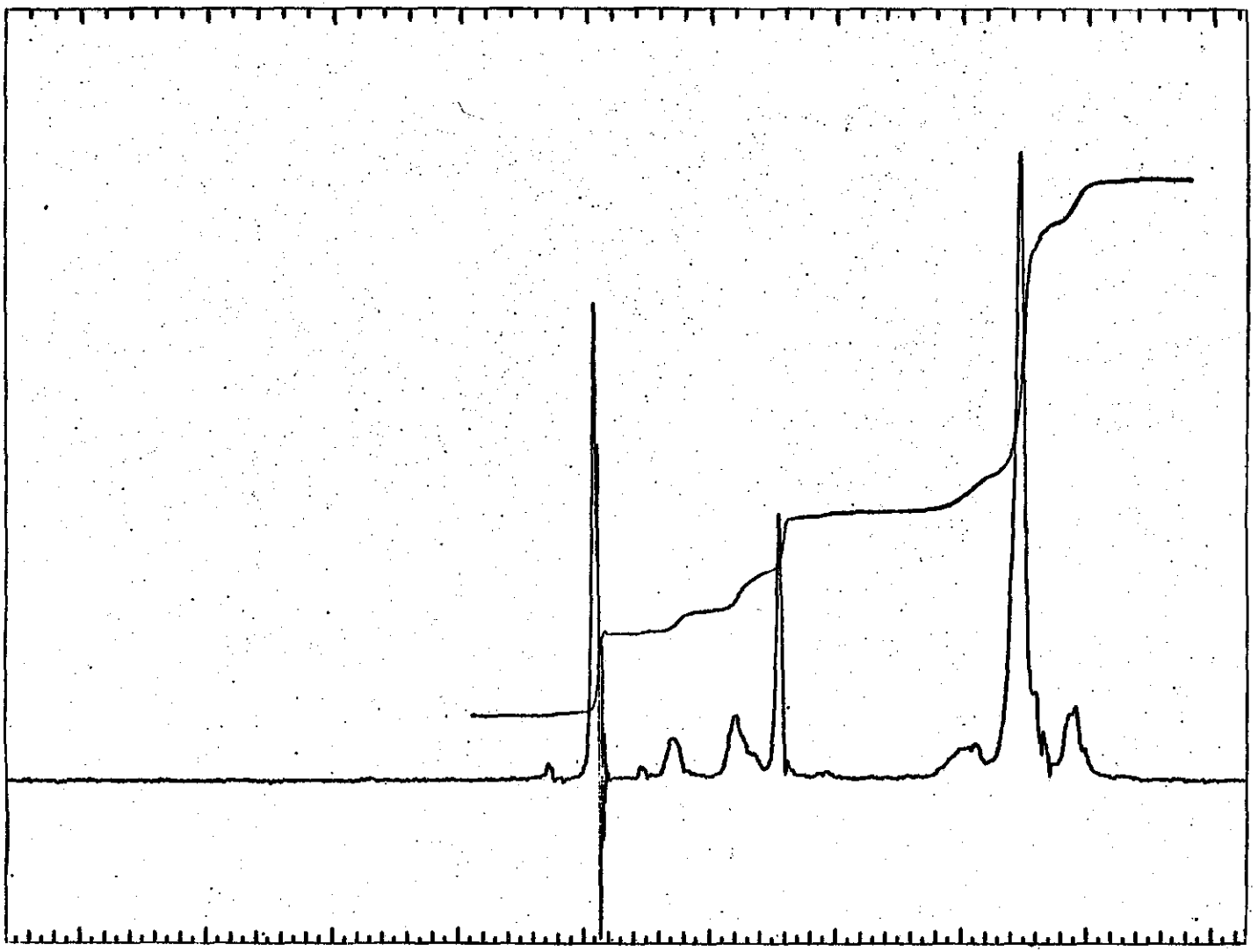
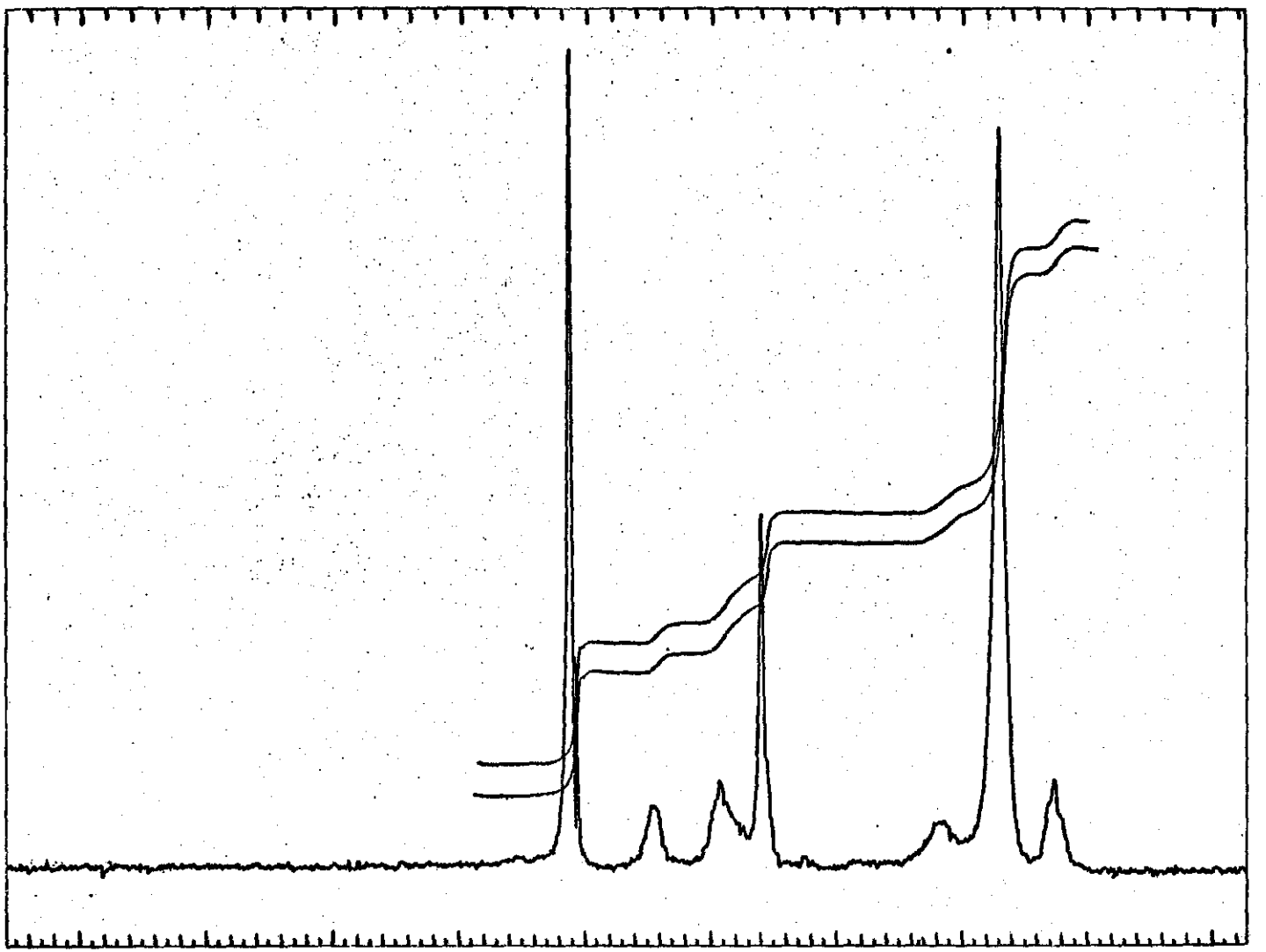


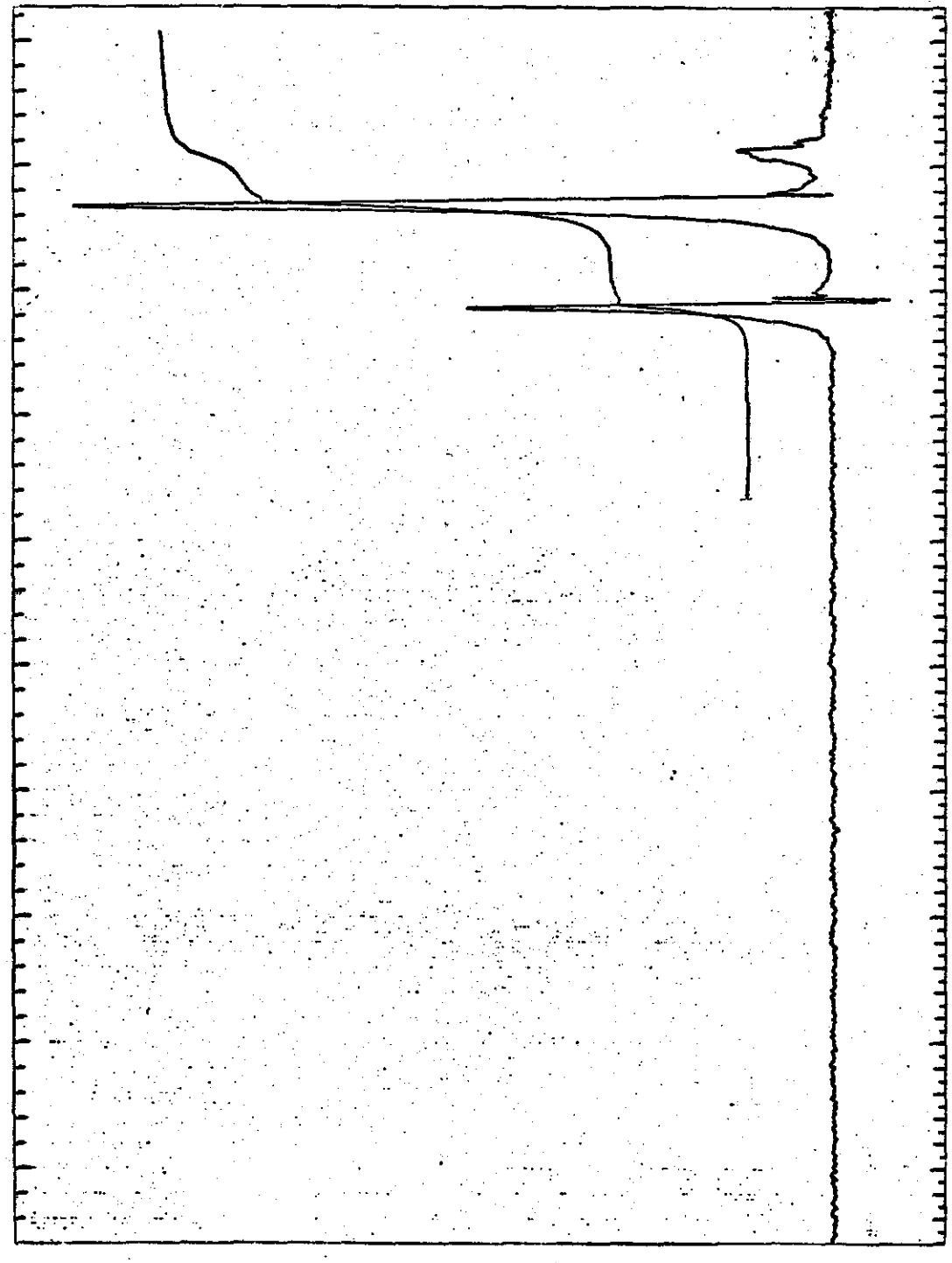
NMR Spectra of N,N-Dimethyl N-[2-hydroxyethyl] dodecylammonium bromide (DDOH, 13)



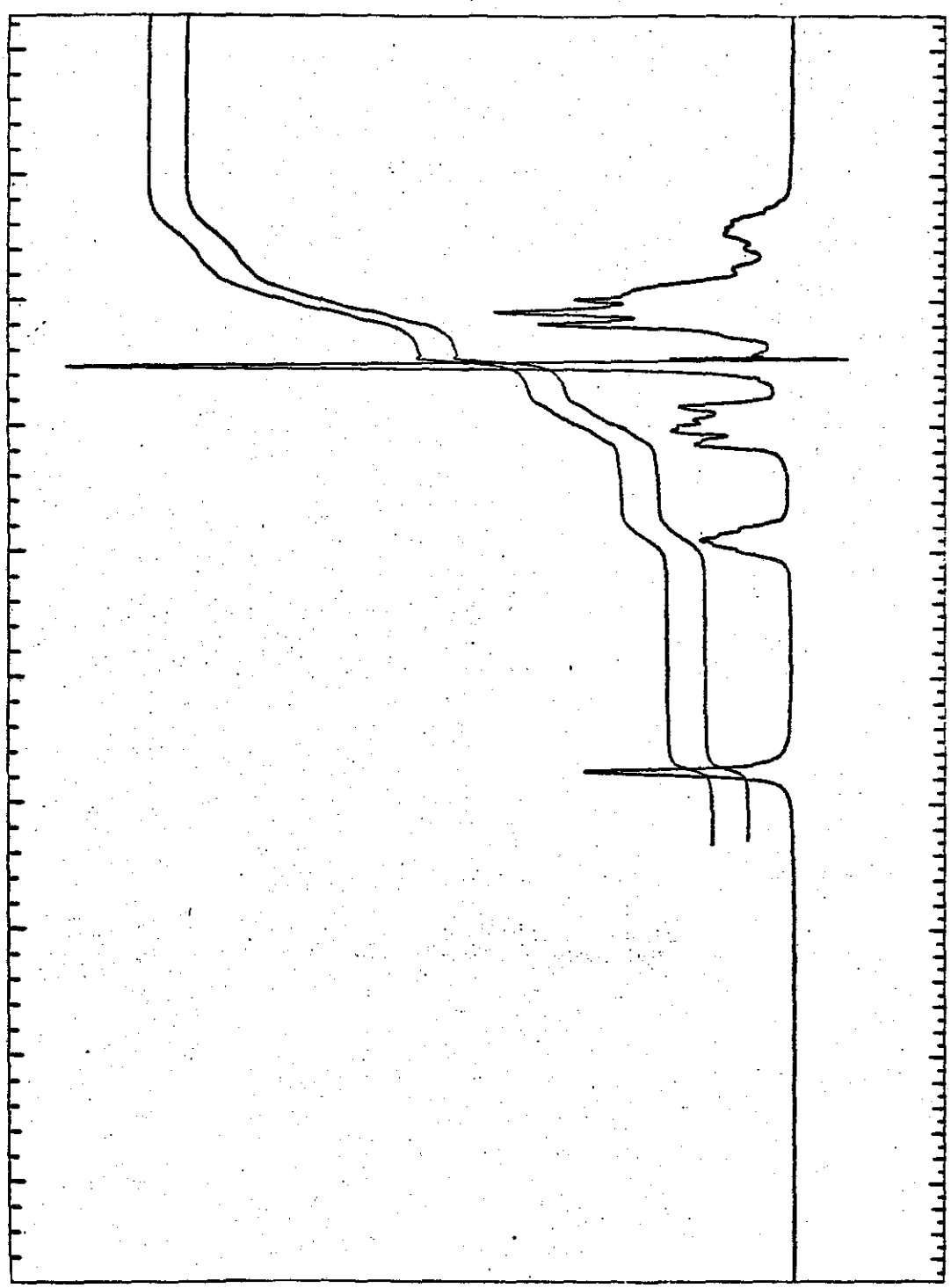
NMR Spectra of N,N-Dimethyl N-[2-hydroxyethyl] hexadecylammonium bromide (CTOH, 14)



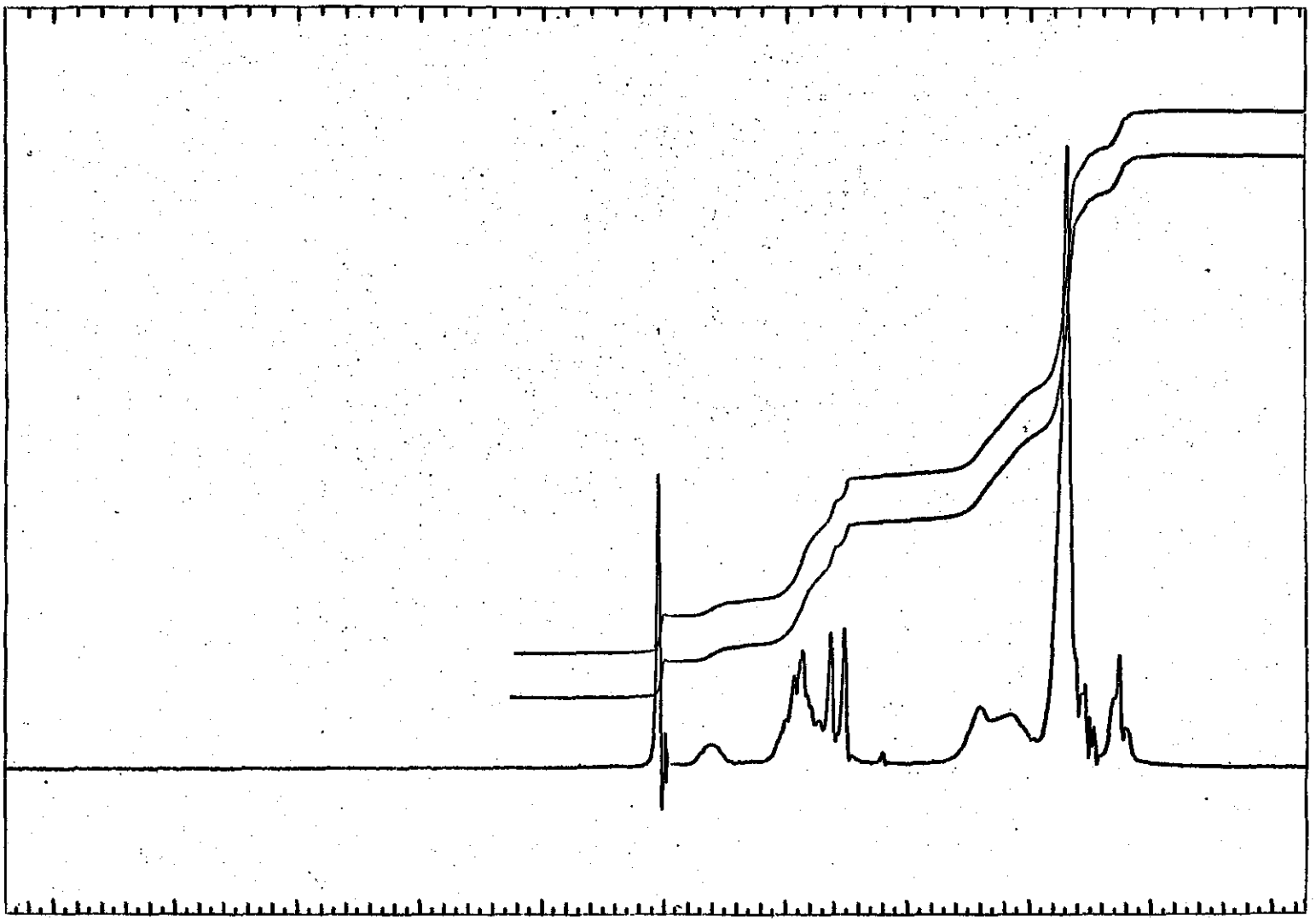
NMR Spectra of N,N-Dimethyl N-[2-hydroxyethyl] dodecylammonium chloride (DDOHCl, 27)



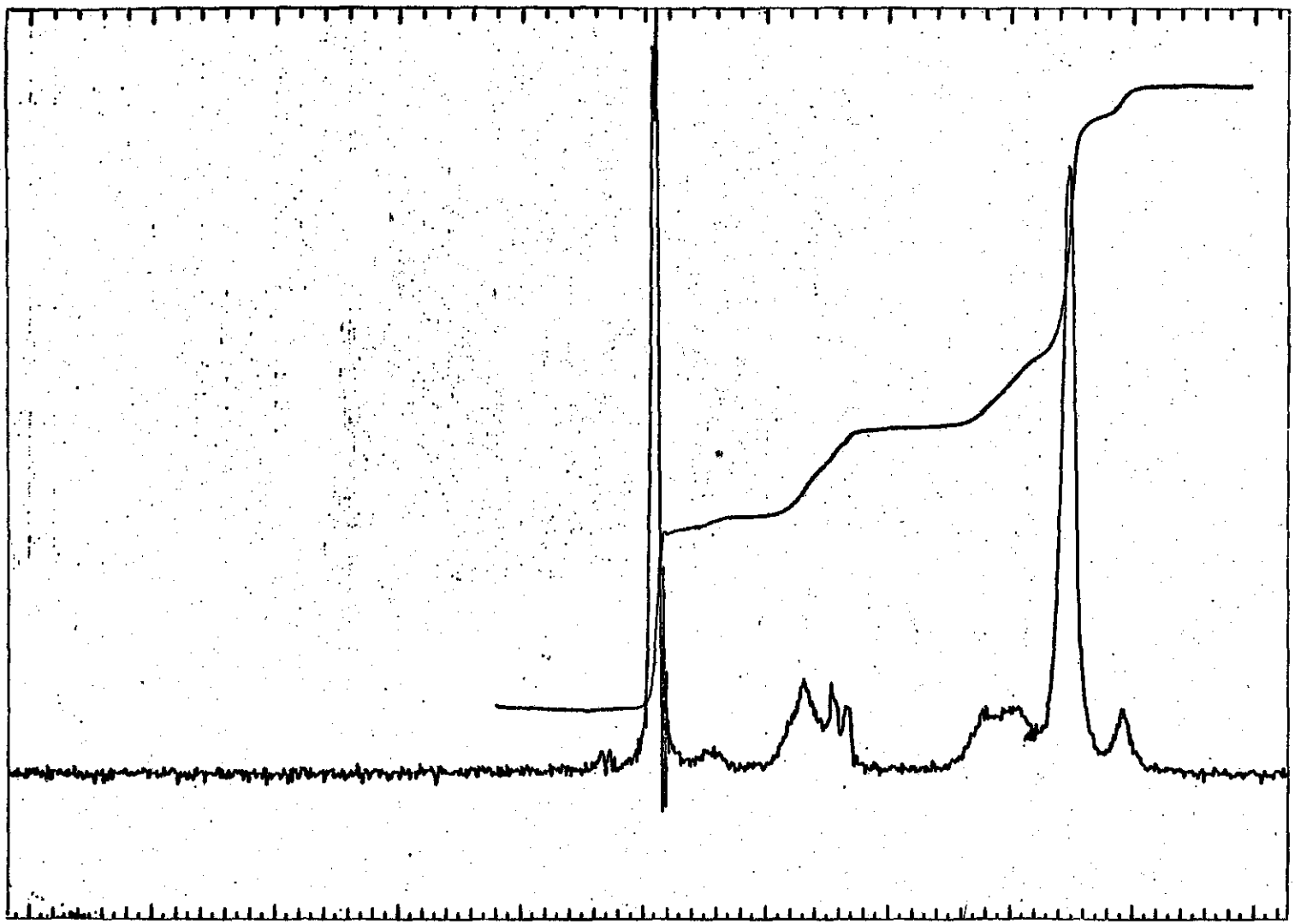
NMR Spectra of N,N-Dimethyl dodecylamine



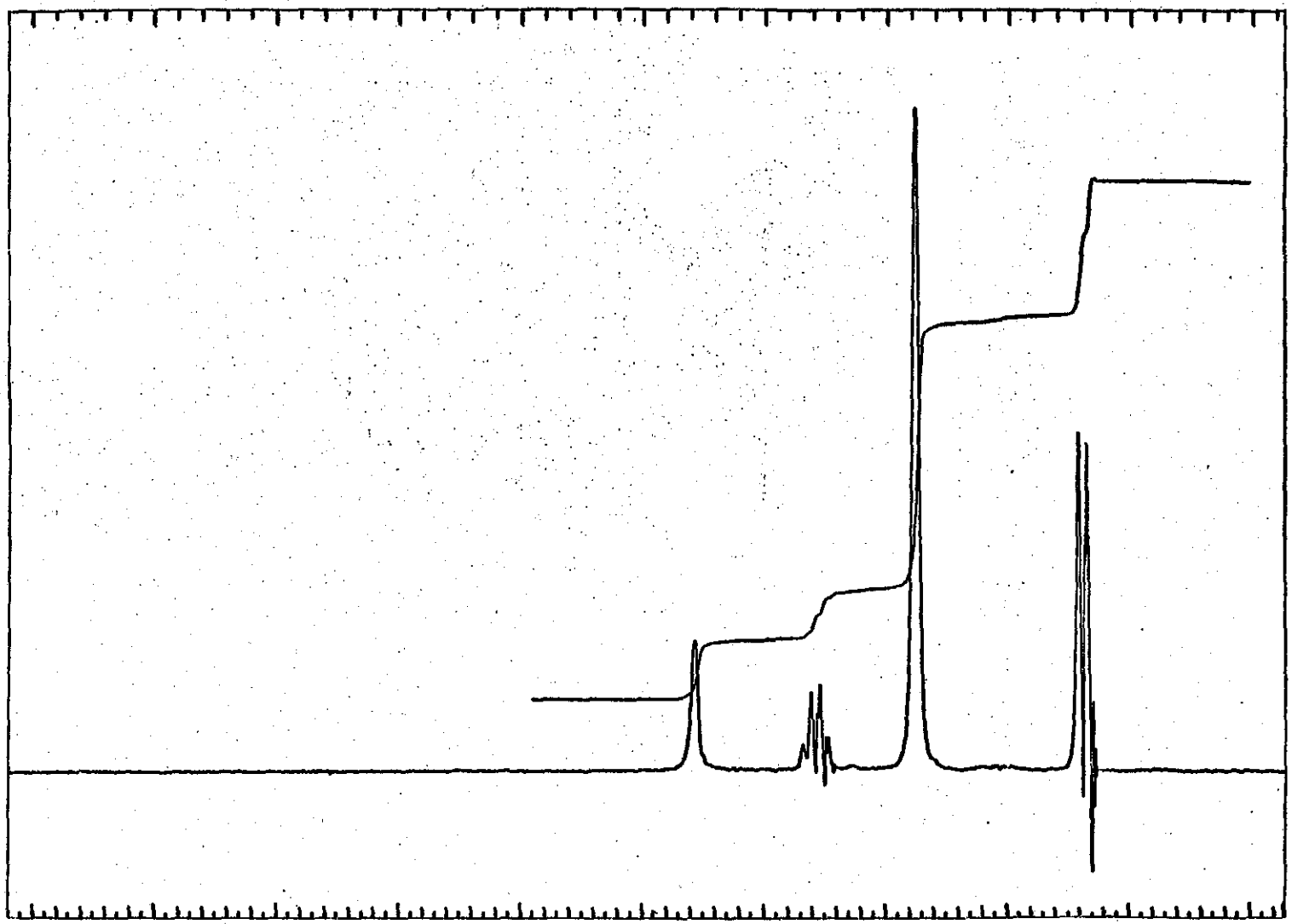
NMR Spectra of 3-Hydroxy N-methyl-piperidine



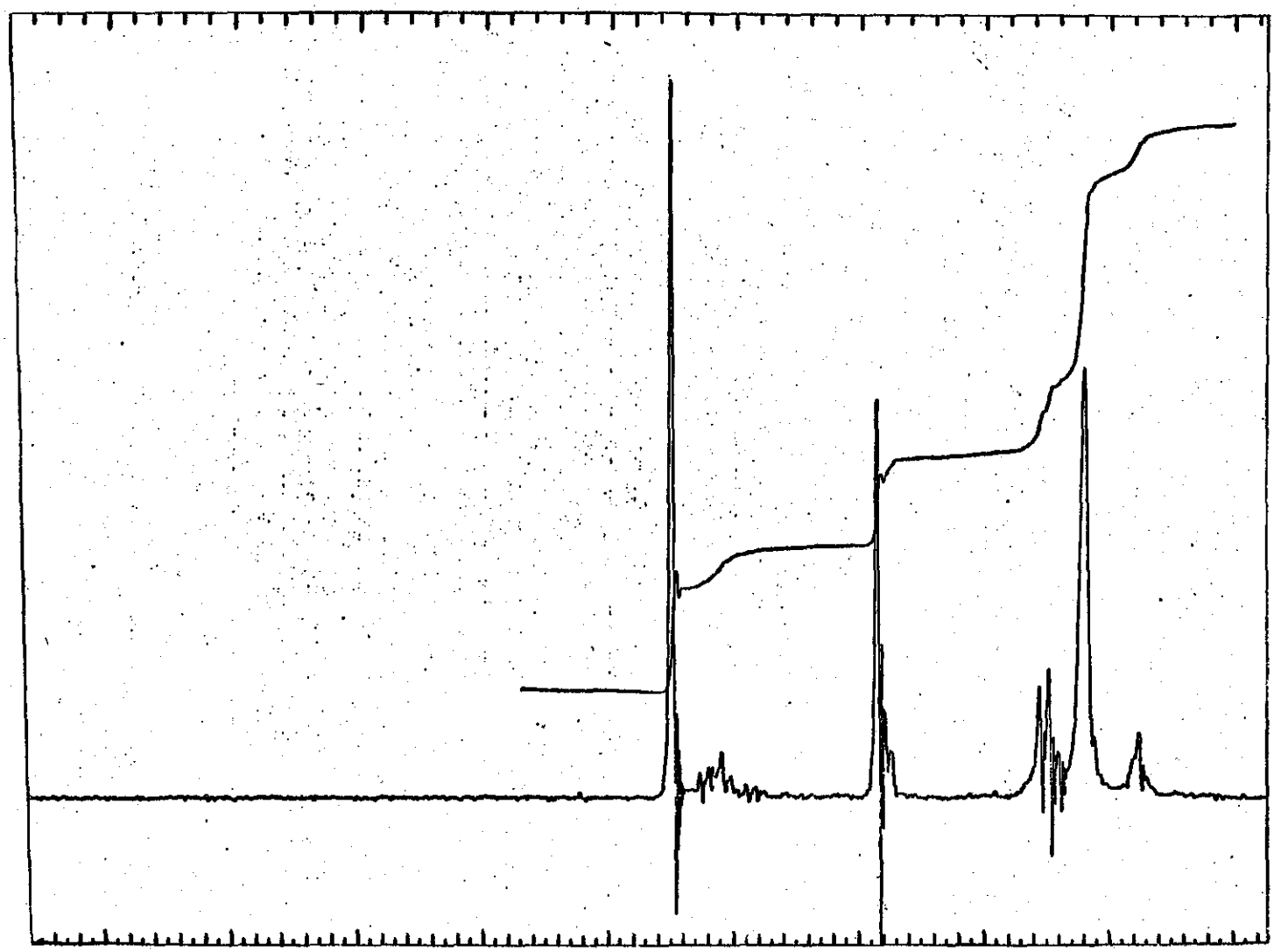
NMR Spectra of N-Methyl N-dodecyl 3-hydroxy-piperidinium bromide (DPBr, 28)



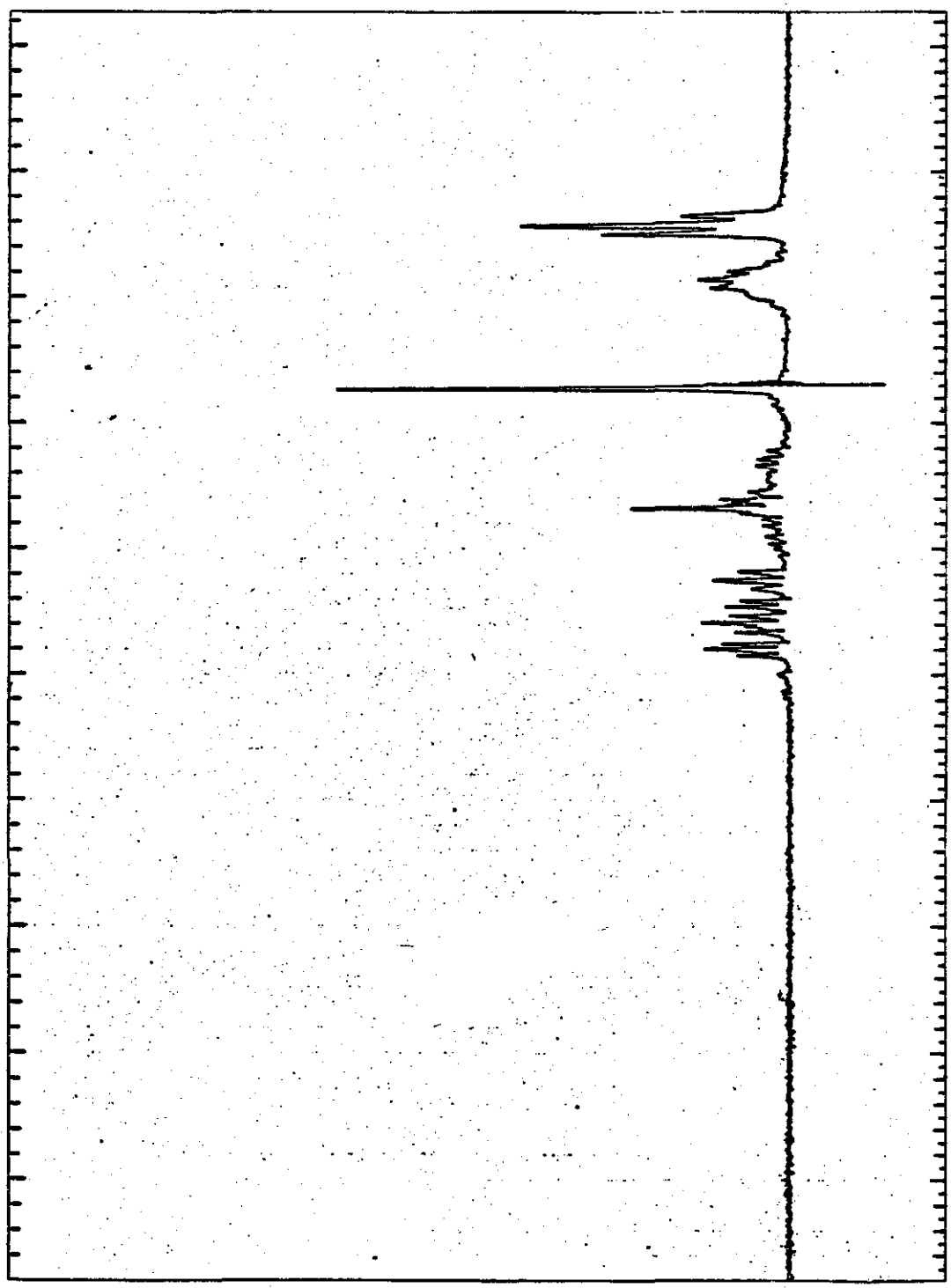
NMR Spectra of N-Methyl N-hexadecyl 3-hydroxy-piperidinium bromide (CTPBr 29)



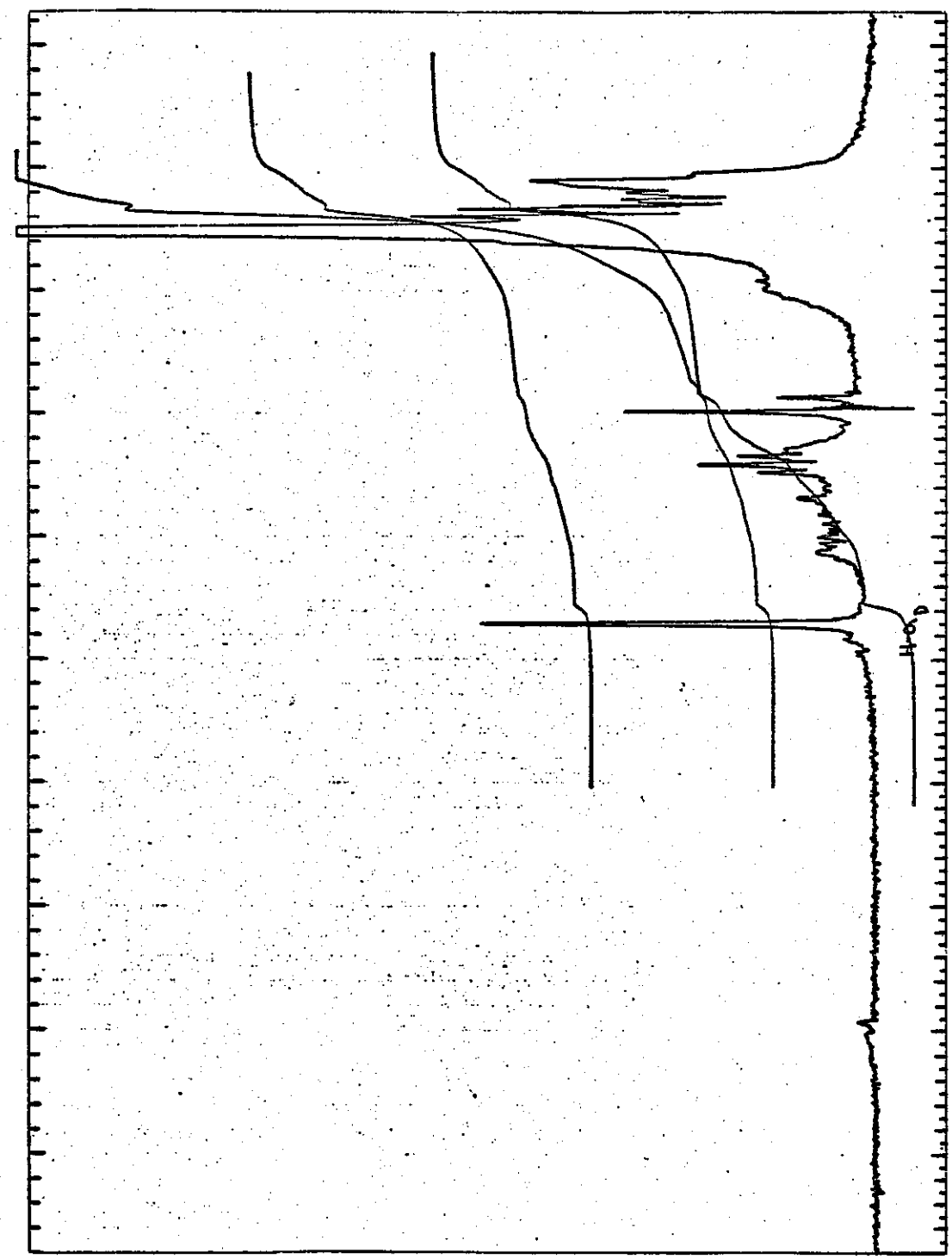
NMR Spectra of N,N-Dimethyl dℓ-alanine



NMR Spectra of N,N-Dimethyl N-dodecyl-dℓ-alanine (23)



NMR Spectra of L-2-Dimethylamino-1-butanol



NMR Spectra of L-2-N-Hexadecyl N,N-dimethylamino-1-butanol bromide